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First-principles study of interaction of molecular hydrogen with Li-doped carbon nanotube peapod structures

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Using first-principles density functional theory based on gradient corrected approach, we have studied interaction of H_2 molecule with Li-doped carbon nanotube and nanotube based peapod structures. We find that H_2 physisorbs on pure carbon nanotube, which is in agreement with earlier studies, and this binding increases when H_2 binds to Li-decorated on carbon nanotube surfaces: the binding is further enhanced with Li atoms deposited on C_{60} doped nanotube peapod structures. The increase in binding in the latter structures arises due to charge transfer between the nanotube and C_{60}, which further facilitates charge transfer from Li to the nanotube. Encapsulating fullerene molecule inside the nanotube provides a different way of increasing charge concentration on Li atom adsorbed outside the nanotube. The increase in H_2 binding energy due to C_{60} encapsulation, compared to recently engineered metal doped nanotube structures, may lead to different carbon based materials for hydrogen storage at room temperature.

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Carbon based materials show promise for effective hydrogen storage.[1] In particular, nanoscale carbon structures such as carbon nanotube, fullerenes, and carbon nanofibers, due to their large surface area, have attracted much attention as molecular hydrogen storage materials for meeting U.S. Department of Energy (DOE) target of 9 wt % and 81 g/l (Refs. 2–10) for the year 2015. While early experimental studies showed large H_2 wt % for single walled carbon nanotube, subsequent experiments find that the H_2 wt % for pure carbon nanotube structures may not exceed 1 wt %.[11–13] One of the primary reasons for these conflicting results is that the binding of H_2 on carbon nanotube surface is van der Waals in nature (binding energy range from 20 to 100 meV) and the wt % could be easily changed with slight change in experimental conditions such as temperature and pressure in experiments and/or presence of other molecules such as H_2O/OH.[14–16] Recently, attempts have been made to increase the binding of H_2 with functionalized carbon nanotube. Yildirim and Ciraci, for example, considered Ti decorated carbon nanotube surface and found that binding of H_2 improves considerably to 7 wt % of hydrogen storage capacity.[17] Similar conclusions are found when Ti is decorated on fullerene structures. While this approach opens an avenue for storing hydrogen with a good wt %, the work was based on the assumption that Ti prefers to coat the nanotube surface as monolayers without clustering. Sun *et al.*, however, showed in a recent paper that Ti indeed prefers to cluster on these surfaces thereby not being effective in increasing the binding of H_2 to the Ti-doped nanotube: the clustering, in addition, reduces the wt % for hydrogen storage in these doped systems.[18] They also showed that when Li atoms are decorated on fullerenes, they rather prefer to stay as atoms on these surfaces and clustering of Li atoms is energetically highly unfavorable.[19] Subsequently, Sun *et al.* showed that hydrogen molecule binds to the Li on nanotube surface with binding energy of 0.075 eV/H_2 with 13 wt %.[19] These results suggest that Li-doped carbon nanostructures may not only improve molecular hydrogen interaction with the material but also give higher wt %. Subsequently, Cabria *et al.* have studied interaction of H_2 with Li-doped graphene and carbon nanotube using first-principles density functional method.[20] The authors in both the above papers[19,20] find that while the binding energy of H_2 with Li doped system increases compared to pure carbon systems, the interaction energy (~100 meV) is below what would be required for room temperature hydrogen adsorption and desorption process (~300 meV) as needed by DOE.

In this Brief Report, we have studied interaction of H_2 with Li-doped carbon nanotube peapod structures using first-principles density functional method. We find that binding of H_2 with Li deposited on peapod complex is increased substantially compared to that on Li-doped carbon nanotube and is about eight times that on pure nanotube structure. The increase in binding arises due to charge transfer from nanotube to encapsulated fullerenes, which, in turn, increases charge transfer from Li to nanotube surface. This makes Li more positively charged, resulting in stronger charge induced dipole interaction between H_2 and Li. The large increase in H_2 binding with carbon nanotube based peapod structures compared to that with the previous carbon nanotube based structures suggests a different class of systems for future hydrogen storage materials. The remaining of this Brief Report is organized as follows. In the next section, we present the computational details. In Sec. III, we present our results followed by the conclusions in Sec. IV.

Our calculations are based on first-principles density functional method. In particular, we have used generalized gradient approximation (GGA) of Perdew and Wang (PW91)[21] for exchange and correlation functional. The calculations are based on supercell approach and the wave functions are expanded using plane waves. The ionic cores are replaced by ultrasoft pseudopotentials[22] and the accuracy of pseudopotentials scheme is tested for carbon system by comparing the results with that obtained using projector augmented wave method.[23] We have used an energy cutoff of 330 eV and the Monkhorst-pack scheme for *k*-point sam-

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TABLE I. Comparison of accuracy of DFT method with MP2 results for H_2 interaction with graphite surface.

Method	Graphite H_2 distance (Å)	Binding energy (meV)
MP2[a]	~3	90
Present calculation based on DFT	3.07	23

[a] Reference 26.

pling. The total energy is converged within 0.01 meV. The calculations are carried out using VASP code.[24] It is important to point out here that H_2 interaction with metal ion complexes arises due to different types of interactions such as electrostatic interactions, orbital interactions, and long range dispersion interactions. As shown recently by Lochan and Head-Gordon in a detailed study, these detailed interaction contributions to the total interaction energy differ for different metal ions.[25] While first-principles density functional theory (DFT), in principle, should account for all these contributions, in practice, the present exchange correlation functionals are unable to account for long range dispersion interactions completely. In order to find out the accuracy of our density functional theory calculations for describing H_2 interaction with graphite, we have compared our results with that of Moller-Plesset (MP2) perturbation based calculations—MP2 theory is known to better describe this interaction including dispersion contribution. Table I shows a comparison of our DFT results with that of MP2 method.[26] One finds here that while the geometrical parameters between the two schemes are in good agreement with each other, the binding energy of H_2 molecule with graphite obtained from DFT method is much less compared to that of MP2 results. This is expected as mentioned earlier due to the absence of long range dispersion interaction in the present functionals, and hence our results will provide a lower bound of H_2 interaction on nanopeapod structures. We are not able to use MP2 method for our study of H_2 interaction with peapod structure since these calculations are computationally demanding. The remaining results are obtained using density functional method.

First, we compute interaction of H_2 molecule with pure carbon nanotube. We have considered the (10, 10) nanotube with diameter of about 1.4 nm. This is the smallest nanotube that could accommodate a fullerene C_{60} molecule as has been observed in experiments. We have optimized the structure of H_2 on the nanotube surface and found that the lowest energy structure is H_2 bonded to the nanotube surface where molecular axis is parallel to the nanotube axis. The binding energy of H_2 on nanotube surface is defined as

$$E(H_2) = (\text{total energy of nanotube with } H_2) - (\text{energy of pure nanotube}) - (\text{energy of } H_2).$$

The binding energy for a parallel orientation is found to be 25 meV as compared to the perpendicular orientation (molecular axis is normal to the nanotube axis) binding energy of 30 meV. These values are lower bound for molecular interaction with nanotube, and based on our estimate, the dispersion energy, which is missing in our DFT method, may provide additional binding energy of the order of 45 meV. This interaction energy is still much smaller compared to the required binding energy of the order of 300 meV for room temperature adsorption and desorption of hydrogen storage process. These results are in good agreement with previous studies and suggest that pure nanotube may not be a good candidate for H_2 storage purposes at room temperature and atmospheric pressure. As mentioned earlier, experimental and theoretical results have recently been carried out to investigate whether metal doped carbon structures such as graphenes, fullerenes, and nanotubes could enhance H_2 interaction. While early experiments suggested larger wt % (20 wt %) for alkali metal coated nanotube,[27] subsequent results find much smaller capacities of these doped nanotube structures.[28,29] We have carried out interaction of Li on (10, 10) nanotube surface and found that the lowest energy configuration corresponds to Li binding on the outside to the center of hexagon ring. The binding energy of Li defined as

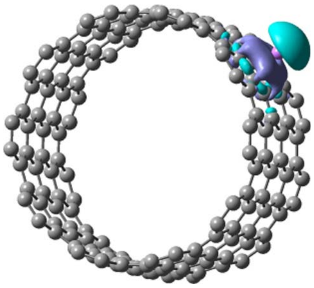

FIG. 1. (Color online) Charge density redistribution plot for Li coated (10, 10) nanotube. $D=D$[Li−carbon nanotube (CNT) complex]$-D$(CNT)$-D$(Li). Blue and purple represent positive and negative charge distributions correspondingly.

$$E(\text{Li}) = (\text{total energy of Li-nanotube complex}) - (\text{energy of nanotube}) - (\text{energy of Li})$$

is found to be 1.64 eV. This binding strength is different from that binding Li on graphene (1.20 eV within GGA functional[29]) but is comparable: the small difference arises due to the curvature effect. Indeed, the Li binding energy on C_{60} surface is found to be about 1.80 eV, again demonstrating the effect of curvature on the energetics: the larger the curvature, the higher the binding energy is. The stronger binding of Li compared to molecular hydrogen on the nanotube surface is due to noticeable charge transfer from Li (about 0.4*e*) to the nanotube. Figure 1 shows a redistribution of charge density plot for Li-nanotube complex where one finds excess electron charge density on nanotube surface particularly near the atoms close to Li. Now, we bring the H_2 molecule close to the Li atom on the nanotube surface. We have studied various hydrogen binding sites near Li atom: (a) on top of Li atom, (b) on top of C–C bond along the zigzag direction, (c) on top of C–C bond along the armchair direction, (d) on top of C atom, and (e) in the center of hexagon ring adjacent to Li-hexagon ring (along the tube axis and perpendicular to the tube axis, not shown here). For each binding site, we take two different H_2 orientations: tangential and normal to the nanotube surface. We found four different local minimum structures with similar binding energies. The

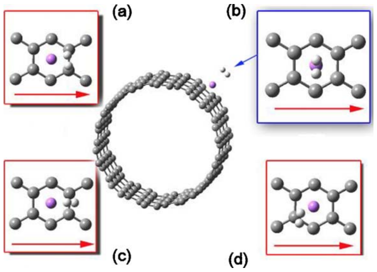

FIG. 2. (Color online) Ball and stick picture of optimized structures of H_2 (white balls) on Li (magenta) coated (10, 10) nanotube (gray carbon atoms). Upper right (b) blue structure is an enlarged local top view of center geometry, where hydrogen molecule is on the top of Li atom with its H-H bond parallel to the nanotube surface. Red arrow indicates the tube axis. The other three lowest energy structures are shown in red frame where the hydrogen molecule is binded, (a) with H-H bond tangential to the CNT surface and on top of the C-C bond along the armchair direction, (c) with H-H bond normal to the CNT surface and on top of the C-C bond along the armchair direction, and (d) with H-H bond tangential to the CNT surface and on top of one C atom.

ball and stick structures for these configurations are shown in Fig. 2. One of these configurations is similar to the undoped nanotube surface, as mentioned before. The binding energy of H_2 on the Li-nanotube complex is found to be around 180 meV—about 150 meV larger compared to that of the undoped nanotube. The increase in binding is due to charge induced dipole interactions originating from charge transfer between Li and nanotube. It is interesting to point out that in contrast to earlier work by Cabria *et al.*, where they find that H_2 binds to the carbon atom on the nanotube surface, our result suggests that lower energy structure also includes where the H_2 binds to Li atom on the nanotube surface. It is equally interesting to point out that H_2 binding to the bare Li^+ ion is much stronger (0.26 eV) (Ref. 30) compared to that on Li-doped nanotube. This could be rationalized due to the fact that Li on nanotube surface has much reduced localized charge (about 0.42e). Similar conclusions have been observed in metal ion complexes where the charge on Li atom is reduced substantially compared to its bare charge configuration.[25] These results suggest that physisorption of H_2 on nanotube could be enhanced due to doping in the system, but binding energy is still below what is required for room temperature hydrogen storage purpose. One key understanding that has come out from this and other works is that charge transfer plays an important role on the H_2 binding. This suggests that if we could improve further the charge transfer from Li to nanotube surface, we may be able to further increase the H_2 binding. We have recently shown that in fullerene doped carbon nanotubes, known as peapod structures, charge transfer occurs from the nanotube to the fullerene encapsulated inside the nanotube.[31] In order to study how this could affect our hydrogen binding on the subsequent Li-doped compound, we have carried out extensive calculations for this complex. We have optimized first the peapod structure where C_{60} molecule is encapsulated inside the (10, 10) nanotube. Subsequently, Li is adsorbed on the resulting peapod structure: we have tried Li on different positions on the nanotube surface (outside) such as on top, bridge, and center positions. The lowest energy structure corresponds to where Li binds to the center of the hexagon on the nanotube surface. The structure is similar to that on nanotube without C_{60}—however, the binding energy of Li,

$$E(\text{Li}) = (\text{energy of Li-doped peapod structure}) - (\text{energy of peapod}) - (\text{energy of Li}),$$

is found to be 1.76 eV. The Li binding energy on the pure nanotube surface is 1.64 eV. The additional 0.12 eV increase in binding of Li to the nanotube surface is also reflected in the decrease of the distance between Li and nanotube surface in the nanopeapod structure (1.71 Å) compared to that in pure nanotube case (1.76 Å). The noticeable increase in binding of Li to the nanotube surface results from charge transfer from nanotube to the C_{60} molecule, which, in turn, facilitates further charge transfer from Li to nanotube. A charge analysis finds the charge on Li atom in the peapod structure to be 0.51e compared to 0.42e in the pure nanotube case. It is helpful to recollect here that C_{60} inside the nanotube acquires about 0.62e from the nanotube.[31] This makes the nanotube positively charged which helps further charge transfer from Li to nanotube surface. We then bring H_2 molecule toward the peapod complex for the study of the resulting interaction. Again, there are four different binding structures which correspond to a similar lowest energy. The optimized structure of the complex is shown in Fig. 3. Notice that these four configurations are different from those in Fig. 2. The most important result of this Brief Report related to structural and energetics information of H_2 interaction with the peapod structure is provided in Table II. The binding energy of H_2 molecule within GGA approximation is found to be 217 meV as compared to ~180 meV value of binding energy of H_2 on pure Li-nanotube complex. This noticeable increase in H_2 binding on the peapod complex is due to increased charge transfer from Li to the nanotube which is further facilitated by charge transfer from nanotube to the C_{60} molecule trapped inside the nanotube. We also studied

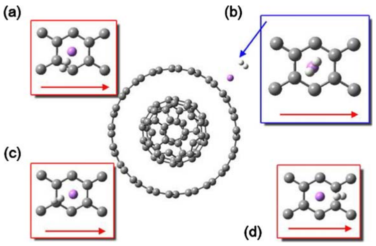

FIG. 3. (Color online) Optimized structure of H_2 on Li coated (10, 10) nanotube containing C_{60} molecule inside (nanopeapod structure). Upper right (b) blue structure is an enlarged local top view of center geometry, where hydrogen molecule is on top of Li atom with its H-H bond tangential to the CNT surface. Red arrows indicate tube axis. The other three lowest energy structures of hydrogen binding are shown in red frame, (a) with H-H bond normal to CNT surface and on top of C-C bond along the zigzag direction, (c) with H-H bond normal to CNT surface and on top of C atom, and (d) with H-H bond normal to CNT surface and on top of C-C bond along the armchair direction.

the various binding sites of H_2 molecule on nanopeapod structure without Li doped on the outside surface and found the binding energy to be 55 meV. Note that this value is also larger compared to similar structures without C_{60} doped inside (~30 meV). This increase in binding energy is directly due to charge transfer between C_{60} and nanotube. Although the binding energy of H_2 molecule obtained from our calculations are still below the required 300 meV value for room temperature hydrogen purpose, the computed binding is much larger than that of any nanotube based structures studied so far. In addition, our computed value of binding energy represents the lower bound of the "true" binding energy due to lack of dispersion interaction in the present GGA functionals (see Ref. 32 and Table I in this Brief Report). Indeed, the dispersion energy for this system could account additional contribution; in that case, the H_2 binding energy with peapod may fall within the required room temperature value for hydrogen storage materials. It is also possible to dope peapod structure with other metals such as K whose ionization potential is lower than that of Li where the increase in charge transfer could be larger compared to that in Li which could make H_2 interaction stronger. Additionally, it will be of great importance for the study if this increase trend in binding energy of H_2 with peapod structures persists for more than one H_2 molecule, particularly for achieving the required wt % for meeting DOE target. Clearly, future theoretical and experimental works are necessary to address these issues.

In summary, we have carried out first-principles density functional calculations based on gradient corrected functional of H_2 interaction with pure nanotube, Li-doped nanotube, and Li-doped nanotube peapod structures. Our results show that H_2 molecule weakly binds to the nanotube surface without doping, and binding is enhanced with Li-doped nanotube surface. We find four different binding structures which result in a similar binding energy, and the increase in H_2 binding is due to the direct interaction between Li ion and H_2 molecule. The molecular binding energy on Li-doped nanotube is much smaller compared to that on the bare Li^+ and is in agreement with other metal ion complexes. This is due to the fact that the charge of Li atom on Li-nanotube complex is about 0.4*e* as compared to +1*e* charge on bare Li ion. Encapsulating C_{60} molecule inside the nanotube provides a different way of increasing charge concentration on Li adsorbed outside the nanotube surface. We find noticeable charge transfer from nanotube to the C_{60} molecule which facilitates further charge transfer from Li to the nanotube—this makes Li deposited on peapod structure more positive (the Mulliken charge on Li is found to be about 0.5*e*). These results show further increase in H_2 binding: the H_2 binding energy on the Li coated peapod structure is found to be over 0.21 eV within GGA approximation. Our computed binding energy provides a lower bound of the true binding energy due to lack of long range dispersion interaction in the present GGA functionals. The increase in H_2 binding energy due to C_{60} encapsulation provides a different way of enhancing H_2 binding which may lead to different carbon based materials for hydrogen storage at room temperature (ideal binding energy for this should be around 300 meV). In addition, doping with other metals such as K whose ionization potential is lower than that of Li may provide better materials for hydrogen storage. Other issues such as if the enhanced binding energy in peapod structure persists with additional hydrogen molecules (i.e., binding energy per molecule remains on the order of 200–300 meV) and if nanopeapod structures could provide required gravimetric wt % will be interesting to explore in future studies.

TABLE II. Binding energy of Li and Li-nanotube surface distance on nanotube and nanopeapod structures. Also, the binding energy of H_2 molecule and H–Li bond distance on nanotube and nanopeapod structures.

System studied	Distance (Å)	Binding energy
Li on nanotube	1.76	1.64 eV
Li on nanopeapod	1.71	1.76 eV
H_2 on Li coated nanotube	2.10	180 meV
H_2 on Li coated nanopeapod	2.08	217 meV

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