Interaction between hydrogen molecules and metallofullerenes

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Within first-principles density functional theory, we explore the feasibility of using metallofullerenes as efficient hydrogen storage media. In particular, we systematically investigate the interaction between hydrogen molecules and La encapsulated all-carbon fullerenes, C_n ($20 \leq n \leq 82$), focusing on the role of transferred charges between the metal atoms and fullerenes on the affinity of hydrogen molecules to the metallofullerenes. Our calculations show that three electrons are transferred from La atom to fullerene cages, while the induced charges are mostly screened by the fullerene cages. We find the local enhancement of molecular hydrogen affinity to the fullerenes to be sensitively dependent on the local bonding properties, rather than on the global charging effects. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3197006]

I. INTRODUCTION

In recent years, tremendous research efforts have been made in exploring hydrogen as a potential energy carrier for efficient, clean, and renewable energy resource.[1,2] However, there are still challenges for practical application of hydrogen fuel. One of them is to find an optimum hydrogen storage medium, where high capacity of hydrogen can be stored in reversible ways. Various classes of materials have been investigated so far as potential candidates for storing hydrogen. Among them metal-coated nanocarbon materials,[3–6] for example, are one of the widely studied materials. Various coating elements have been investigated so far to enhance chemical reactivity of carbon surfaces, thus they can attract hydrogen molecules more effectively. Alkali metals can attract significant amount of hydrogen molecules as they are coated onto nanocarbon materials, such as carbon fullerene surfaces,[3] while their binding strength is not high enough to ensure reversible hydrogen storage at near-ambient conditions. On the other hand, transition metal doped nanocarbons can generate chemically very active sites to hydrogen, where reversible hydrogen storage is possible.[4,5] However, the challenge there is how to achieve a uniform metal coating onto nanocarbon surfaces.[7–9] Recently, alkaline earth metals such as Ca is suggested as a superior coating element to all the considered coating elements in functionalizing carbon nanostructures,[6] where the above problems with other elements can be resolved.

Endohedral metallofullerenes ($M @ C_n$), which consist of one or more metal atoms (M) inside the hollow space of fullerenes (C_n), are novel forms of fullerene-base materials.[10–15] Different types of fullerenes with encapsulating different types of metals such as alkali metal, group 2, and 3 metal as well as lanthanoid, have been

synthesized.[10–15] One of the interesting features of this material is the induced charges to fullerenes upon metal encapsulation. For example, lanthanum metallerenes have charge states of $La^{3+} @ C_n^{3-}$,[10–15] which can be viewed as a positively charged core metal surrounded by a negatively charged carbon cage.[11] Since the number of transferred charge is large, it may enhance the hydrogen binding to a metallofullerene comparing to a pristine fullerene.

In this paper, we explore the feasibility of using metallofullerenes as efficient hydrogen storage media using *ab initio* density functional approaches. In particular, we systematically studied the interaction between molecular hydrogen and La encapsulated all-carbon fullerenes, C_n ($20 \leq n \leq 82$), focusing on the role of transferred charges between metals and fullerenes on the affinity of hydrogen molecules. Our calculations show that 3 electrons are transferred from La atom to fullerene cages, while the induced charges are effectively screened by the fullerene cages. We observed the local enhancement of hydrogen binding strength to metallofullerenes and the hydrogen binding strength varies in a wide range depending strongly on the local charge arrangement.

The paper is organized as follows. Our calculation methods and model systems are described in Sec. II. In Sec. III we perform structure optimization of metallofullerenes and analyze their electronic structures, focusing on their charge distribution. In Sec. IV we study molecular hydrogen interaction with metallofullerenes and compare the results with the case of pristine carbon fullerenes. Section V for discussion and conclusion.

II. CALCULATION METHODS AND MODEL SYSTEMS

Our total energy calculations are based on *ab initio* density functional theory, with employing a plane-wave basis set and projector-augmented wave pseudopotentials.[16,17] We compared our results from two different types of exchange-correlation potentials, Ceperley–Alder version of local den-
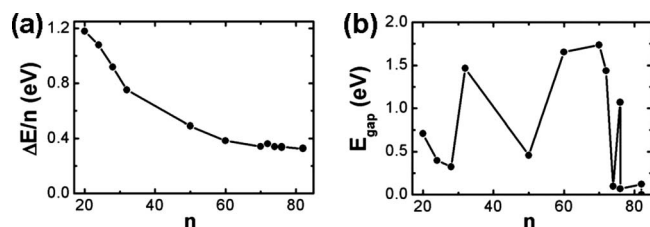
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FIG. 1. Formation energies per carbon atom (a) and HOMO-LUMO gaps (b) of different carbon fullerenes, C_n ($20 \leq n \leq 82$). The formation energy is defined as the total energy required to form a structure with respect to that of a graphene.

sity approximations (LDA),[18] and the Perdew–Wang version of the gradient generalized approximation (GGA).[19] Wide ranges of fullerenes were considered in this study; C_n with their symmetries of $n=60$ (I_h), 70 (D_{5h}), 72 (D_{6d}), 74 (D_{3h}), 76 (T_d and D_2), and 82 (C_{2v} and C_{3v}). Also, smaller fullerenes ($n<60$) such as $n=20$ (I_h), 28 (T_d), 32 (C_2), and 50 (D_{5h}), were considered. The detailed geometry of each fullerene can be found elsewhere.[10] We study metallofullerenes containing La atom inside the hollow space of fullerenes, La@C_n as a prototype of metallofullerenes. The $5s5p6s5d$ electrons of La are treated as valence electrons. The energy cutoff for the plane-wave basis set of 400 eV and a cubic supercell of $22 \times 22 \times 22$ Å^3, allowing a vacuum size of at least 14 Å between buckyballs were considered. All considered structures were relaxed, without any constraints, until the force on each atom was less than 0.01 eV/Å.

III. OPTIMIZATION OF METALLOFULLERENES AND CHARGE REDISTRIBUTION

We performed full relaxation of different types of all-carbon fullerenes (C_n). Their formation energy is presented in Fig. 1(a), where the formation energy is defined as the total energy required to form a structure with respect to that of a graphene. Small fullerenes have relatively high formation energy, thus less stable. It is due to the fact that they cannot satisfy the isolated pentagon rule.[20]

We introduced a La atom inside each fullerene and carefully optimized the location of La atom inside each cage. We found that C_{20} is too small to contain a La inside, where all-carbon atoms form strong chemical bonds with the La atom centered in the cage. For small fullerenes ($n \leq 32$), the optimized La locations are at the center of fullerenes, while off-centered for large fullerenes ($n \geq 50$). Our finding is consistent with previous experiments reporting C_{36} as the smallest possible metallofullerene with La.[21] For the most extensively investigated metallofullerene, La@C_{82}, we confirmed that C_{82} with C_{2v} symmetry is the most favorable structure among its isomers to encapsulate a La inside.[12] The optimized La atom is off-centered by 1.956 Å toward the hexagonal ring along the C_2 axis of C_{82} (C_{2v}) isomer, which is well compared with the experimental values of 1.969 Å.[13,14] The nearest La–C distance is 2.511 Å, in good agreement with the experimental value of 2.588 Å and theoretical values.[12–15] The fully optimized geometries are displayed on the left panels of Fig. 2(a).

Local density of states (LDOS) of metallofullerenes are presented in Fig. 2(c), in comparison to those of pristine fullerenes in Fig. 2(b), where the yellow-dotted lines representing Fermi levels E_F. For large metallofullerenes La@C_n ($n \geq 50$), the La $4f$, $5d$, and $6s$ states are located above the Fermi level and its valence states ($5s$ and $5p$ states) are located far below E_F, beyond the energy range in the panels of Fig. 2(c). Upon the encapsulation of a La atom, the Fermi levels shift up and the occupancy of fullerene lowest unoccupied molecular orbital (LUMO) levels occurs. For instance, the LUMO level of C_{82} which is located at -4.74 eV becomes fully occupied and the LUMO+1 at -4.23 eV [bottom panel of Fig. 2(c)] being half-filled after the encapsulation of La atom [see the bottom panels of Figs. 2(b) and 2(c)]. This is a strong indication that there are three valence electrons ($6s^25d^1$) transferred from La to the carbon-related states[12–15] and the charging states is represented by La^{3+}@$C_n{}^{3-}$ for fullerenes for $n \geq 50$.[11] For smaller fullerenes ($n<50$), such as La@C_{28} and La@C_{32}, La–C hybridized states present below E_F due to the small size of the fullerene and the resulting stronger coupling between La and the nearest carbon atoms, indicating less than three electron charge transfer.

We observe that the amount of transferred charges sensitively depends on the position of La atom inside the fullerenes. For instance, if La atom is kept fixed at the center of C_{50}, there are some La–C hybridized states presented near E_F (not shown here), indicating less than three electrons transferred from La to C_{50}.[22] Previous theoretical calculations have shown that there are only two electrons transferred to the carbon cage if La atom is located at the center of C_{82}.[23] Considering the size of the fullerene (~ 7 Å in diameter), the amount of transferred charge is large, which may enhance the hydrogen binding energy to metallofullerene.[24]

IV. INTERACTION BETWEEN MOLECULAR HYDROGEN AND (METALLO)FULLERENES

We considered different hydrogen adsorption sites on fullerenes and metallofullerenes and found no strong dependence on the adsorption sites. Figure 3 shows the binding energy of a single hydrogen molecule located on top of a hexagonal ring of each fullerene, which is a preferred hydrogen site. The displayed results are taken from the highest values from different hexagon sites of each fullerene. Their binding energies calculated from LDA or GGA are shown in Fig. 3. Hydrogen binding energy is generally higher if the gap between the highest occupied molecular orbital (HOMO) and LUMO is lower. The low HOMO-LUMO gap (E_g) ($E_g \leq 0.2$ eV) fullerenes are such as C_{28} (T_d), C_{74} (D_{3h}), C_{76} (T_d), and C_{82} (C_{2v} and C_{3v}), as shown in Fig. 1(b). However, the binding is still too weak to be utilized for hydrogen storage;[3] the hydrogen binding energies range from 0.07 to 0.10 eV or from 0.02 to 0.04 eV depending on LDA or GGA, respectively.

Next, we consider interactions between a hydrogen molecule and metallofullerenes. Upon the introduction of a hydrogen molecule to the La encapsulated C_{20} the dissociative
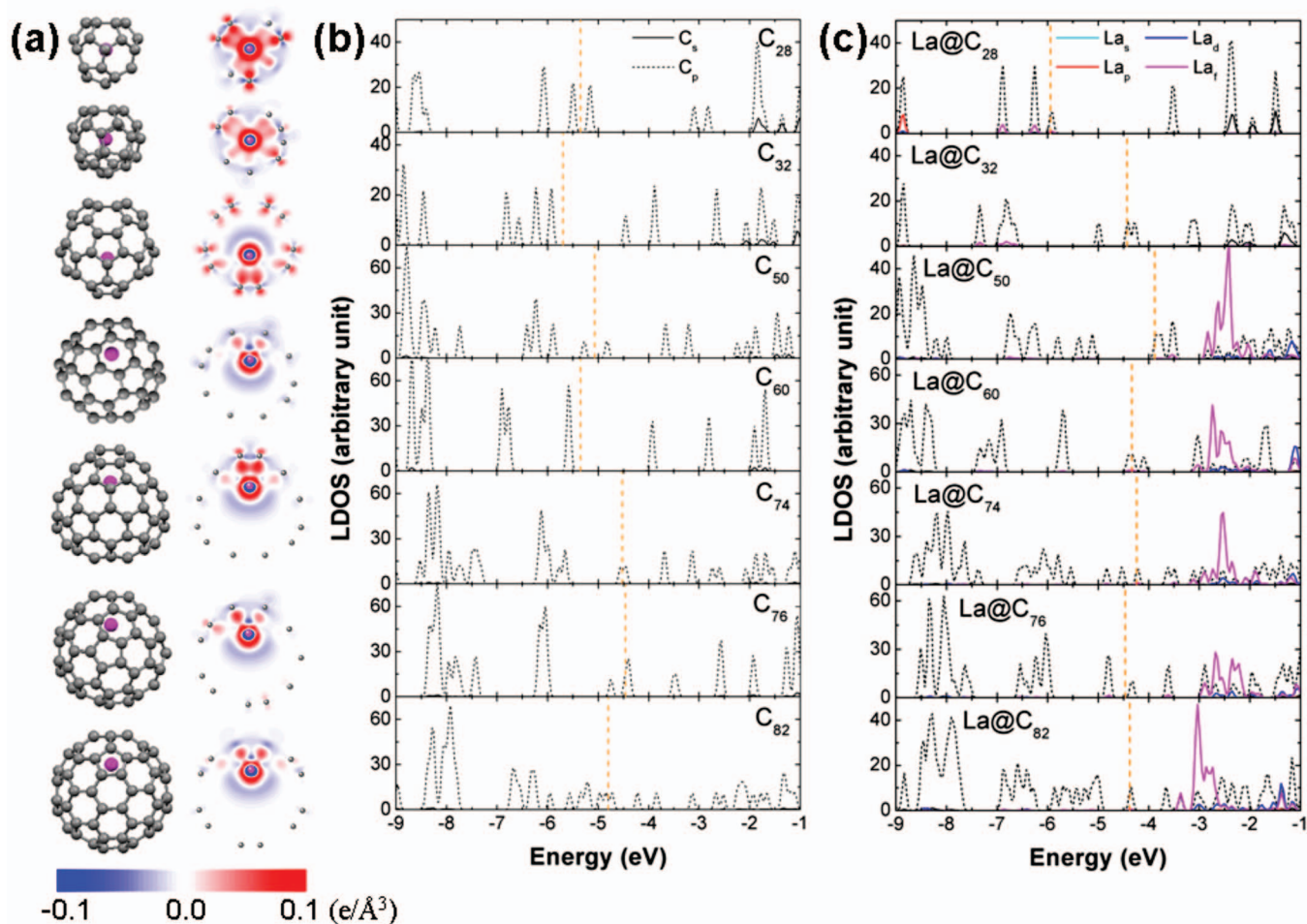
FIG. 2. The optimized $La@C_n$ complexes displayed in the left panels of (a) and their difference charge densities ($\Delta\rho$) are shown in the right panels. The difference electron charge density are defined as $\Delta\rho = \rho(La@C_n) - \rho(C_n) - \rho(La)$. The transferred electrons from a La atom to a carbon cage are highly localized inside a cage and very small density of charges are dispersed outside of the cage. The LDOS of pristine fullerenes (b) and metallofullerenes (c) are compared. For large fullerenes ($n \geq 50$) three extra electrons are occupied at the carbon-related states and the charging states become $La^{3+}@C_n^{3-}$. For smaller fullerenes, less than three electrons are transferred from a La atom to a cage due to strong chemical coupling between a fullerene and a La atom. The charge densities are in the unit of $e/\text{Å}^3$ and the dotted-yellow lines stand for Fermi level.

adsorption of a hydrogen molecule occurs, which breaks up the C_{20} cage after a few optimization steps. We found that hydrogen molecule has a strong binding to these small structures due to rich in electron density at the adjacent pentagon regions. For example, we found that the smallest fullerene, C_{20}, which completely consists of pentagons, is chemically extremely active; A hydrogen molecule is dissociated and makes strong chemical bond to the fullerene in a atomic form with a binding energy of 3.22 eV/H_2.

On larger fullerenes C_n ($n > 20$) the hydrogen molecule is adsorbed in a molecular form. The greatest hydrogen binding enhancement is found on C_{50} surface, where the LDA hydrogen binding energy increases from 0.068 to 0.090 eV/H_2 upon La encapsulation. We observed the slight elongation of hydrogen bond length from 0.769 to 0.770 Å, while the distance between the hydrogen molecule and the hexagonal ring is decreased from 2.744 to 2.690 Å, indicating a stronger interaction of hydrogen molecule with $La@C_{50}$ than with pristine C_{50}. When the hydrogen molecule is adsorbed near the hexagon along the C_2 axis of pristine C_{82}, H_2 binds to the fullerene with 0.085 eV energy gain and the hydrogen bond length is 0.770 Å, very close to

the calculated value of 0.767 Å for an isolated hydrogen molecule. The distance between hydrogen molecule and the carbon hexagon ring is 2.647 Å. The hydrogen binding energy on $La@C_{82}$ is similar. Also, the hydrogen bond length and the distance between hydrogen and the hexagon are 0.768 and 2.777 Å, respectively, indicating a weaker interaction than that of H_2–C_{82}. In most cases, the geometry of hydrogen molecule has no significant change upon the La
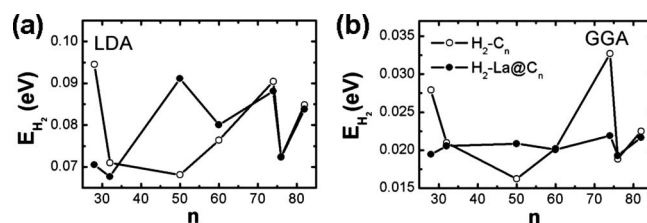

FIG. 3. Binding energies of a hydrogen molecule to either pristine fullerenes (empty points) or metallofullerenes (solid points). The calculations performed by LDA (a) and GGA (b) are compared. We considered different hydrogen adsorption sites and found no strong dependence on the adsorption sites. The displayed results are taken from the highest values from different hexagon sites of each fullerene.
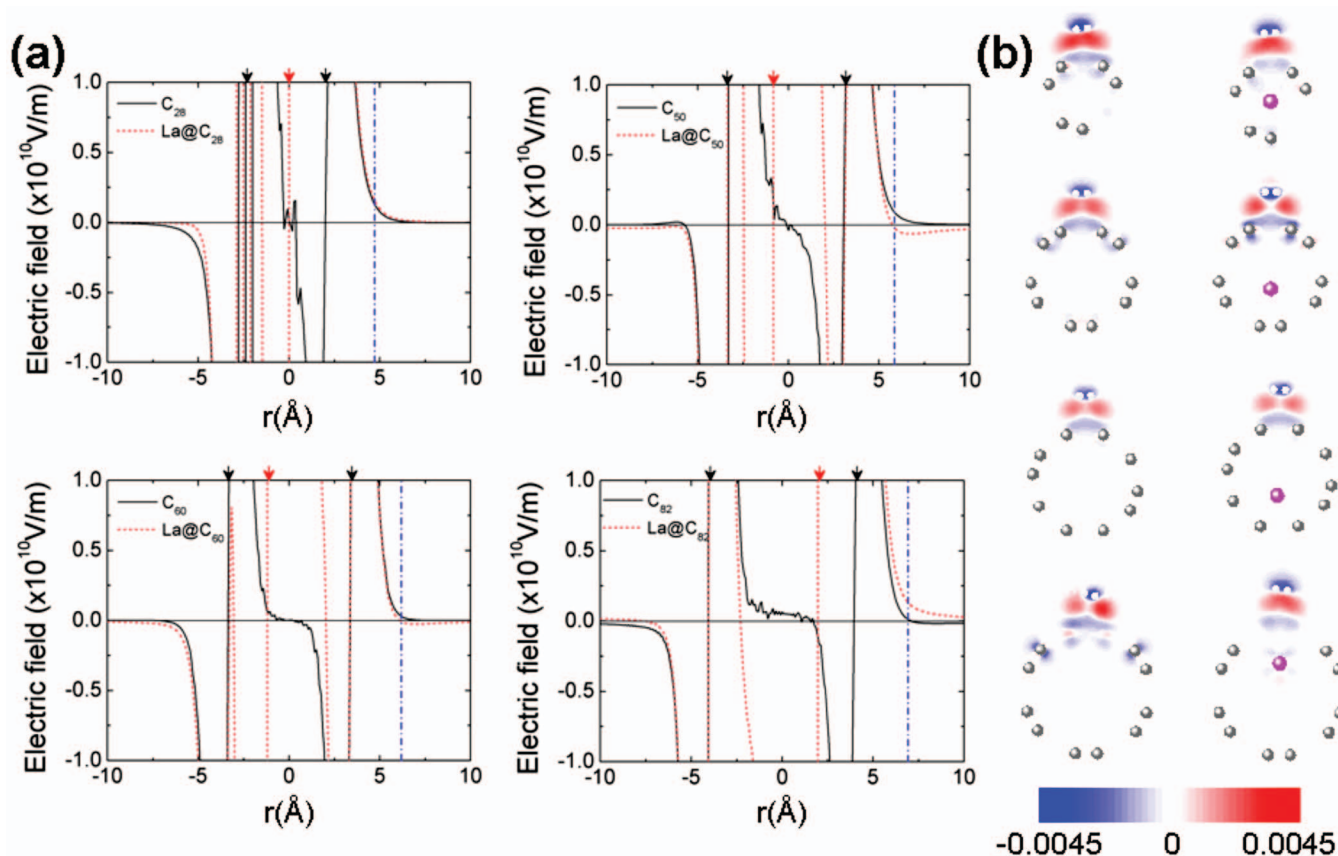
FIG. 4. (a) Electric fields produced by metallofullerenes (red-dashed lines) and pristine fullerenes (black lines) of $n=28$, 50, 60, and 82. The black arrows indicate the location of carbon cages and the red arrow the La location. (b) The charge differences of a hydrogen molecule are displayed. Here, the difference charge densities ($\Delta\rho$) are shown in the right panels. The difference electron charge density are defined as $\Delta\rho=\rho(H_2-C_n)-\rho(C_n)-\rho(H_2)$ or $\Delta\rho=\rho(H_2-La@C_n)-\rho(La@C_n)-\rho(H_2)$, where the charge densities are in the unit of $e/Å^3$.

encapsulation. The hydrogen binding energy is not significantly enhanced or even decreases by encapsulating a La atom inside the fullerene, despite of the high charge transfer to fullerene cages. Moreover, the enhancement of the hydrogen binding energy shows no clear relationship with the properties of the fullerene and metallofullerene, rather highly depends on the local structures.

We investigate the reasons of no significant enhancement of hydrogen affinity to metallofullerenes regardless of high charge transfer. First we consider the physical location of transferred charges by La encapsulation. In the right panels of Fig. 2(a) the difference electron densities of metallofullerenes, defined as $\Delta\rho=\rho(La@C_n)-\rho(C_n)-\rho(La)$, are presented. We find that La@C_{50}, which has the greatest hydrogen binding enhancement, shows a high electron accumulation over the C_{50} surface upon the metal encapsulation. However, overall, the transferred charges are rather localized inside and near the La atom and very small density of charges are dispersed out side of fullerenes. Interestingly, there is even electron depletion near and outside the fullerene. This observation is in stark contrast to the common knowledge that the carbon cage in metallofullerene is treated as a negatively charged object by which the transferred charges are thought to be delocalized on the cage,[11,22] and the amount of net charge gain in the carbon cage is negligible.

Because of the localization of the transferred charge and

the screening of the carbon cage, the electric field produced by the metallofullerenes is very weak regardless of the high charge transfer from La to a cage. The calculated electric fields of several pristine fullerenes (black lines) and metallofullerenes (red-dashed lines) ($n=28$, 50, 60, and 82) are displayed in Fig. 4(a). The black arrows indicate the location of carbon cages and the red for the La atom. The electric field produced at the optimum hydrogen molecule location (indicated by the dotted-blue lines), which is about 2.7 Å from the fullerene, is close to zero on both pristine and metallofullerene, resulting in a similar polarization and binding energy of hydrogen molecule. The tiny difference in electric field may be obtained by local electronic structures. Thus the hydrogen molecule cannot experience the large amount of transferred charges. Not only the amount of charges but also the charging methods are important to enhance the hydrogen binding energy.

We further calculate the difference electron charge density of hydrogen molecule on fullerenes and metallofullerenes. The results for $n=28$, 50, 60, and 82 are presented in Fig. 4(b). The difference electron charge density is defined as $\Delta\rho=\rho(H_2-C_n)-\rho(C_n)-\rho(H_2)$ or $\Delta\rho=\rho(H_2-La@C_n)-\rho(La@C_n)-\rho(H_2)$. Due to the lower electronegativity than carbon, the hydrogen molecule is slightly polarized on fullerenes, with electron accumulation near the carbon cage and electron depletion on the opposite side. It is clear from

Fig. 4(b) that the polarization of the hydrogen molecule is quite similar on both fullerenes and metallofullerenes. The polarization of the hydrogen molecule slightly changes upon La encapsulation. In some cases such as La@C_{50}, the hydrogen molecule has a larger polarization, while in other cases may has a smaller polarization, depending on the specific charge redistribution on a given site. This electric field is not strong enough to improve H_2 affinity beyond the physiosorption nature. In this case, the dispersion interactions between H_2 and fullerenes are important and van der Waals corrections have to be included in order to accurately describe the H_2 and fullerene interactions. This is a missing component in LDA and GGA functionals and we plan to include such corrections in the future study.

In a previous work, we demonstrated that the hydrogen binding energy on charged fullerenes can reach up to 0.32 eV/H_2.[24] The enhancement of the binding energy of hydrogen molecule on a charged fullerene is due to the high polarization of the hydrogen molecule under the strong electric field produced by the charged fullerene. We found that metallofullerene is quite different from a charged fullerene, although there is a high intrafullerene charge transfer. Since the polarizability of a hydrogen molecule is small, a strong electric field as high as 10^{10} V/m is necessary to reach a hydrogen binding energy of 0.3 eV/H_2.[24] However, the metallofullerene is not a charged but a neutral system. Far away from the metallofullerene the electric field is essentially zero. On the other hand, the transferred charges from La to the carbon cage may produce a nonzero electric field near the fullerene, which is a short range effect. If the transferred charge is distributed over the outside of a fullerene and thus influences a relatively large region, there may be an electric field high enough near a hydrogen molecule to increase the hydrogen binding energy.

V. DISCUSSION AND CONCLUSION

In this paper, we have investigated molecular hydrogen interaction with pristine and La encapsulated carbon fullerenes C_n ($20 \leq n \leq 82$). Our investigation was to find the possibility of metallofullerenes as a hydrogen storage medium using *ab initio* density functional technique. By encapsulating La inside fullerenes three electrons transfer from the metal atom to the fullerene cage. However, no significant enhancement in hydrogen binding energy was observed by encapsulation a transition metal atom inside the fullerene, despite of the high charge transfer from the metal atom to the carbon cage. Detailed analysis revealed that the transferred charge is localized inside the carbon cage, contrary to the general idea that the transferred charge is delocalized on the carbon cage. Thus we conclude that metallofullerenes are not superior to the pristine fullerenes with respect to hydrogen storage in spite of the high charge redistributions.

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