Functionalized heterofullerenes for hydrogen storage

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Using density functional theory, we show that Li decorated B doped heterofullerene (Li12C48B12) has the following desired properties of a hydrogen storage material. (1) The Li atoms remain isolated. (2) Through charge transfer to electron deficient C48B12 heterofullerene, the Li atoms become positively charged. (3) Each Li atom is able to bind up to three \( \text{H}_2 \) molecules, which remain in molecular form, and the binding energies of successive \( \text{H}_2 \) molecules are in the range of 0.135–0.172 eV/\( \text{H}_2 \), suitable for ambient temperature storage. (4) The gravimetric density reaches the 9 wt % limit necessary for applications in the mobile industry. © 2009 American Institute of Physics. [DOI: 10.1063/1.3058678]

The limited supply of fossil fuels and their adverse effect on the environment due to the emissions of greenhouse gases and volatile organic chemicals have necessitated the search for alternative energy sources that are abundant, renewable, pollution-free, secure, and cost effective. In this regard hydrogen is being considered as a potential candidate. In addition to being the most abundant element in the universe, hydrogen offers many advantages over other fuels. It is nontoxic, clean to use, and packs more energy per unit mass than any other fuel. However, one of the most challenging problems in hydrogen economy is our ability to store hydrogen with high gravimetric and volumetric density at near ambient thermodynamic conditions. It is widely accepted that for technological applications, solid state materials are necessary for storing hydrogen. To meet 9 wt % gravimetric density, storage materials should consist of elements lighter than aluminum, and for near ambient pressure and temperature applications, the binding energy of hydrogen should be in the order of 0.2 eV/\( \text{H}_2 \). Since the energy with which hydrogen is bound in light materials is an order of magnitude higher than the above value, attention has focused on nanostructures of light elements, particularly carbon fullerenes and nanotubes.7–8

It was recently proposed7,8 that decorating carbon fullerenes and nanotubes with transition metal atoms can bind hydrogen in large quantities with binding energies in the ideal range for mobile applications. Later studies, however, showed that homogeneously coated \( \text{C}_{60} \) fullerenes with transition metal atoms are metastable and the transition metals would cluster on the fullerene surface, thus undermining their ability to store hydrogen in large quantities. It was suggested that one can overcome the clustering problem by decorating \( \text{C}_{60} \) with Li atoms,10 but the binding energy of \( \text{H}_2 \) molecules became too low for room temperature applications. The central challenge has been to find metal atoms that will resist clustering and yet bind to hydrogen with binding energy intermediate between physisorption and chemisorption. In this letter we propose such material.

Using first principles calculation, we show that Li coated heterofullerene C48B12 can overcome the difficulties outlined in the above. Note that it was demonstrated a long time ago11 that a Li+ ion can bind to at least six \( \text{H}_2 \) molecules with binding energies between 0.253 and 0.202 eV/\( \text{H}_2 \). In \( \text{C}_{60} \text{Li} \), the charge transfer from Li to \( \text{C}_{60} \) has an electron affinity of 2.66 eV, does allow Li to remain in a nearly +1 charge state and hence bind to hydrogen with a binding energy of 0.18 eV/\( \text{H}_2 \). However, as more Li atoms decorate the \( \text{C}_{60} \) the charge on each Li decreases and so does the binding energy of successive \( \text{H}_2 \) molecules. We show that this situation can be avoided by initially doping \( \text{C}_{60} \) with B. In C48B12Li12, Li atoms not only remain isolated but also can each bind up to three \( \text{H}_2 \) molecules with binding energies between 0.172 and 0.135 eV/\( \text{H}_2 \), leading to a gravimetric density of 9 wt %, suitable for ambient temperature storage.1

The chemistry of \( \text{C}_{60-n}\text{B}_n \) clusters is governed by their electron deficient character. Past calculations12 showed that the electron affinities of \( \text{C}_{60-n}\text{B}_n \) clusters (\( n=1–12 \)) are larger than that of \( \text{C}_{60} \) and behave as electron acceptors. Thus, it is expected that when Li atoms decorate the fullerene surface, charge transfer to electron deficient \( \text{C}_{60-n}\text{B}_n \) clusters may leave them in a more positively charged state than that in \( \text{C}_{60} \). We have studied the equilibrium stability and geometry of Li12C48B12 cluster and its ability to adsorb hydrogen using density functional theory and generalized gradient approximation for exchange and correlation. We used a super cell approach where the cluster was surrounded by 15 Å of vacuum space along \( x, y, \) and \( z \) directions. The \( \Gamma \) point was used to represent the Brillouin zone due to the large supercell. The total energies and forces and optimizations of geometry were carried out using a plane-wave basis set with the projector augmented plane wave method as implemented in the Vienna ab initio simulation package (VASP).13 The PW91 form was used for the generalized gradient approximation to exchange and correlation potential. The geometries of clusters were optimized without symmetry constraint using conjugate-gradient algorithm. The energy cutoff and the convergences in energy and force were set to 400 eV, \( 10^{-5} \) eV, and \( 1 \times 10^{-3} \) eV/Å, respectively. The accuracy of our numerical procedure for carbon, hydrogen, and boron systems was demonstrated in our previous papers.9,10,14,15

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Past studies showed that due to the curvature and larger C–C bond length of the C_{60} fullerene compared with that of graphite, it is possible to substitutionally dope C_{60} with B. In particular, Xie et al.\textsuperscript{12} studied the geometries and stability of C_{60−n}B\textsubscript{n} clusters for n = 1–12. Experiments performed by Gao et al.\textsuperscript{16} established the existence of C_{60−n}B\textsubscript{n} clusters (n = 1–6). C_{48}B\textsubscript{12} was found to have two low lying isomers with C\textsubscript{n} and S\textsubscript{6} symmetry.\textsuperscript{12,17} The C\textsubscript{n} isomer, found by Xie et al.\textsuperscript{12} to be the ground state structure, has an ellipsoidal structure with one B atom per pentagon and two B atoms preferentially sitting in a hexagon. The distortion of the C_{60} cage induced by doping is not localized to the neighborhood of each of the dopant atom but rather extends throughout the whole cage. Manaa\textsuperscript{17} showed that a S\textsubscript{6} isomer, which includes a distribution of B atoms on the top and bottom of triphenylene-type units and along the equator of C_{60}, is lower in energy than the C\textsubscript{n} isomer. Both isomers, however, are electron acceptors. In agreement with the work of Manaa,\textsuperscript{17} we found that the C\textsubscript{n} isomer is 0.4 eV higher in energy than the S\textsubscript{6} isomer. However, when 12 Li atoms are coated, the complex based on the isomer of C\textsubscript{n} symmetry is 0.3 eV lower in energy. So in the following we focus our discussions on the C\textsubscript{n} isomer.

The equilibrium geometry of C\textsubscript{n} isomer of the C_{48}B_{12} cluster is shown in Fig. 1(a). We find that B doping decreases the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of C_{60} from 1.76 to 0.3 eV in C_{48}B_{12}, thus making the later more metallic than C_{60}. The HOMO is mainly contributed by C atoms [Fig. 1(b)], while the LUMO is from B atoms [Fig. 1(c)]. It is interesting to note\textsuperscript{12} that the changes of average binding energy per atom in C_{60−n}B\textsubscript{n} are not too big when going from n = 1 to n = 12; the corresponding values were found to be 6.77, 6.75, 6.74, 6.73, 6.71, 6.70, 6.67, 6.66, 6.64, 6.63, 6.62, and 6.60 eV, respectively. We have checked the dynamic stability of C_{48}B_{12} via frequency calculations. We found that there is no imaginary frequency for all the modes, suggesting that C_{48}B_{12} is stable. To further confirm the thermal stability of C_{48}B_{12}, we have carried out molecular dynamics simulation by using Nose algorithm\textsuperscript{18} at room temperature (T = 300 K) with 0.4 fs time steps. After 4 ps simulation, we found that the cage geometry of C_{48}B_{12} was still kept.

To determine the equilibrium geometry of Li\textsubscript{12}C_{48}B_{12}, we studied four isomers shown in Fig. 2. The first choice in Fig. 2(a) was to put 12 Li atoms on top of each B atom in C_{48}B_{12}. Upon optimization, however, the Li atoms migrated to the top of the pentagon sites, as was found to be the case in Li\textsubscript{12}C_{60}.\textsuperscript{10} To check if clustering of Li atoms would occur, we used three cluster configurations [Fig. 2(b)–2(d)]. From the optimized structures we see that the clustered configurations are higher in energy by 7.355, 7.942, and 8.718 eV, respectively, as compared to the isolated configuration [Fig. 2(a)]. It is important to note that in Li\textsubscript{12}C_{60} the clustered configuration was only 2.2 eV higher in energy than the isolated configuration. Thus substituting C by B in the heterofullerene further enhances the stability of the isolated configuration.

Li\textsubscript{12}C_{48}B_{12} and Li\textsubscript{12}C_{60} also have quite different electronic structures as shown in Fig. 3. For example, the LUMO of Li\textsubscript{12}C_{60} is mainly from the coating layer of Li, while it is from C and B in Li\textsubscript{12}C_{48}B_{12}.

Next we have studied the absorption of hydrogen molecules on the Li\textsubscript{12}C_{48}B_{12} heterofullerene. We began by placing...
ing one H2 molecule on the top site of each Li [Fig. 4(a)] and then optimized the geometry without any symmetry restriction. We found that hydrogen is bound molecularly with a binding energy of 0.172 eV/H2 but with a slightly stretched H–H bond length of 0.761 Å. The distance between Li and the nearest H atom is 1.99 Å. When we increased the number of H2 molecules to 24 by placing two H2 molecules on each Li site, the binding energy decreased to 0.147 eV/H2, and the bond length of H2 became 0.757 Å. The nearest distance of H from the Li site increased to 2.10 Å. With three H2 molecules placed on each Li site, i.e., a total of 36 H2 molecules, the binding energy decreased to 0.135 eV/H2, with a corresponding decrease in H–H bond length to 0.753 Å. The nearest distance of H from the Li site increased to 2.20 Å. In Table I, we summarize these results. With 36 H2 molecules adsorbed on a Li12C48B12 cluster, the gravimetric density of Li coated C48B12, which has been synthesized experimentally. Unfortunately C48N12 is not a good candidate. Since N atom has one more valence electron than C, C48N12 is an electron-rich complex and behaves like a donor. We have also investigated the hydrogen storage ability of Li coated C48N12, which has been synthesized experimentally. Unfortunately C48N12 is not a good candidate. Since N atom has one more valence electron than C, C48N12 is an electron-rich complex and behaves like a donor.

Since Li atoms prefer to donate their 2s electrons, the structure of Li12C48N12 is very different in geometry and property. In fact, we find that these 12 Li atoms prefer to cluster instead of remaining isolated. Consequently, the ability of Li12C48N12 is severely undermined.

In summary, based on gradient corrected density functional theory, we have shown that Li decorated boron doped C60 heterofullerene has several advantages over Li decorated C60 fullerene for storing hydrogen. (1) Li atoms in Li2C48B12, like that in Li2C60, do not cluster. In addition, the isolated state in the former is energetically far more stable than in the later. (2) B doping of C60 improves the weight percentage of stored hydrogen as B is lighter than C. (3) Since B has one electron less than C, the resulted C48B12 heterofullerene is electron-deficient and behaves like an electron acceptor. This makes it possible for the Li atoms to freely donate their 2s electrons to the heterofullerene, thereby remaining in a positively charged state. (4) Up to three H2 molecules per Li atom can be attached to the Li12C48B12 heterofullerene leading to a gravimetric density of 9 wt %. (5) The average binding energy of H2 molecules lies between physisorption and chemisorption energies and is almost twice as large as that in Li12C60, lending the possibility that B doped C60 fullerenes may be suitable as a hydrogen storage material in ambient temperature.

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TABLE I. Number of H2 molecules x, binding energy $E_b$ (in eV/H2), bond length of H2 $R_{H2}$ (in angstrom), the distance between H2 and Li ions $R_{Li-H2}$ (in angstrom), and the weight percentage wt % for xH2–C48B12Li12 (x = 12, 24, and 36).

<table>
<thead>
<tr>
<th>x</th>
<th>$E_b$</th>
<th>$R_{H2}$</th>
<th>$R_{Li-H2}$</th>
<th>wt %</th>
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<td>12</td>
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<td>0.761</td>
<td>1.990</td>
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<td>6</td>
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<td>36</td>
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<td>0.753</td>
<td>2.200</td>
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