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Theoretical Study of Hydrogen Storage in Ca-Coated Fullerenes

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Abstract: First principles calculations based on gradient corrected density functional theory and molecular dynamics simulations of Ca decorated fullerene yield some novel results: (1) C_{60} fullerene decorated with 32 Ca atoms on each of its 20 hexagonal and 12 pentagonal faces is extremely stable. Unlike transition metal atoms that tend to cluster on a fullerene surface, Ca atoms remain isolated even at high temperatures. (2) $C_{60}Ca_{32}$ can absorb up to 62 H_2 molecules in two layers. The first 30 H_2 molecules dissociate and bind atomically on the 60 triangular faces of the fullerene with an average binding energy of 0.45 eV/H, while the remaining 32 H_2 molecules bind on the second layer quasi-molecularly with an average binding energy of 0.11 eV/H_2. These binding energies are ideal for Ca coated C_{60} to operate as a hydrogen storage material at near ambient temperatures with fast kinetics. (3) The gravimetric density of this hydrogen storage material can reach 6.2 wt %. Simple model calculations show that this density is the limiting value for higher fullerenes.

Introduction

Hydrogen, the least complex and the most abundant element in the universe, is an energy carrier that is expected to play a critical role in a new, decentralized energy infrastructure with many important advantages over other fuels. Unlike fossil fuels such as oil, natural gas, and coal that contain carbon, produce CO_2, contribute to global warming, and have limited supply, hydrogen is clean, abundant, nontoxic, renewable, and packs more energy per unit mass than any other fuel. However, the biggest challenge in a new hydrogen economy is finding materials that can store hydrogen with high gravimetric and volumetric density under favorable thermodynamic conditions and exhibit fast kinetics.[1−7] The current methods of storing hydrogen as compressed gas or in the liquid form does not meet the industry requirements since the energy densities are much lower than that in gasoline. Moreover, there are issues of safety and cost involved in compressing hydrogen under high pressure or liquefying it at cryogenic temperatures.

Although storage of hydrogen in solid state materials offers an alternative, currently there are no materials that meet the industry requirement. This is because materials to store hydrogen with high gravimetric density (e.g., 9 wt %) have to be lighter than aluminum. Unfortunately, in these elements, hydrogen is bound either strongly as in complex light metal hydrides or weakly as in carbon based nanostructures, clathrates, zeolites, and metal organic frameworks.[8−14] The early promise of carbon nanotubes[8] as high density storage materials has not materialized.[15−17] Attention has, therefore, turned to the functionalized carbon fullerenes and nanotubes[18−23] where transition metal atoms uniformly distributed over the surface were shown to bind copious amounts of hydrogen in a quasi-molecular form through a novel mechanism where the adsorbed H_2 molecule donates electrons to the unfilled d-orbitals of the transition metals atoms which in turn back-

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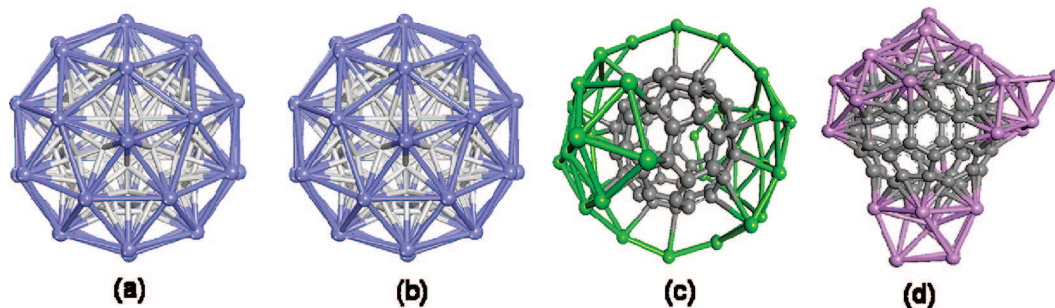*J. Chem. Theory Comput., Vol. 5, No. 2, 2009* **375**

Figure 1. (a) Optimized geometry of $C_{60}Ca_{32}$; (b) geometry of $C_{60}Ca_{32}$ after 5 ps MD simulation; (c) geometry of $C_{60}Mg_{32}$ after 0.4 ps MD simulation; and (d) geometry of $C_{60}Li_{32}$ after 0.5 ps MD simulation.

donate the electron to the antibonding orbital of the H_2 molecule. Consequently, the H_2 molecule does not dissociate but binds quasi-molecularly with a stretched H−H bond. The binding energy of about 0.5 eV/H_2 molecule is in the ideal range for room temperature applications. Later studies[21] showed that these materials are not stable as the strong d-d interaction between transition metal atoms leads to clustering, which greatly affects their hydrogen storing capacity. Although Li atoms in $C_{60}Li_{12}$ do not cluster due to strong Li−C bond and weak Li−Li bond,[22] the absorption energy of H_2 is weak and hydrogen desorbs at low temperatures.

In this study we show that $C_{60}Ca_{32}$ does not suffer from any of these shortcomings. First, it is a very stable cluster whose magicity has been established from gas-phase experiments.[24] Martin and co-workers found this cluster to have a conspicuous peak in the mass spectra which is characteristic of a magic cluster with high stability. Second, Ca atoms show no tendency for clustering. Third, this nanocluster can bind up to 124 hydrogen atoms with an average binding energy in the required range (0.1−1.0 eV) and with a weight percentage that can reach the Department of Energy's 2010 target, namely 6 wt %.

The above results are based on first principles calculations 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 Γ 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 (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP).[25] 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 convergence in energy and force were set to 400 eV, 10^{-4} eV, and 1×10^{-3} eV/Å, respectively. The accuracy of our numerical procedure for C_{60} and hydrogen has been demonstrated in our previous papers.[21,22,26] For the Ca_2 molecule, we obtained the ground-state to be $^1\Sigma_g^+$ with a bond length of 4.20 Å, in good agreement with the experimental value of 4.277 Å.[27]

Our fully optimized geometry of $C_{60}Ca_{32}$ structure without symmetry constraint shown in Figure 1(a) agrees with the previous theoretical study.[28] Here the C−Ca and Ca−Ca

distances are respectively 2.752 Å and 3.681 Å. The bond lengths between C atoms at the pentagon-hexagon and hexagon-hexagon interface are respectively 1.465 and 1.446 Å. To confirm the stability of this structure, we have carried out molecular dynamics simulation by using Nose algorithm[29] at room temperature (T=300 K) with 0.5 fs time steps. After 5 ps simulation, we found that the structure retains its identity. The resulting geometry is shown in Figure 1(b) which, except for some small fluctuations in bond length due to the thermal motion of atoms at finite temperature, is essentially the same as that in Figure 1(a). Based on these results, we can conclude that $C_{60}Ca_{32}$ is indeed very stable. However, the HOMO−LUMO gap of this complex structure is almost zero, and the system is nearly metallic. Thus, the observed stability is not of electronic origin but purely due to the geometric effects,[23,28] which is different from what happened in Ca@C_{60}.[30] To further verify the stability of $C_{60}Ca_{32}$, we also performed simulated annealing from 300 K to 0 K, by starting from the geometry of Figure 1(b). After 5 ps simulations, it recovers back to the structure of Figure 1(a), indicating again that the later structure has high stability.

To further prove that Ca atoms do not cluster on the C_{60} surface as Ti atoms were found[21] to do, we carried out two separate calculations: In the first we placed four Ca atoms on the neighboring hexagonal and pentagonal sites of the C_{60} surface and second, the four atoms forming a tetrahedron. The optimized geometries with these as starting configurations are shown in Figure 2(a,b). Note that the configuration where the Ca atoms form a tetrahedron is 0.79 eV higher in energy than when they occupy the hollow sites on the C_{60} surface, providing ample evidence that Ca atoms do not cluster on C_{60}, and the core−shell-like geometry of C_{60}-Ca_{32} is more stable. In the equilibrium geometry of $C_{60}Ca_{32}$, about 0.4 electrons per Ca atom are transferred to fullerene core. In Figure 3(a) we show these changes in charge distribution where yellow stands for missing charge and blue for charge gained. We also find that HOMO and LUMO originate mainly from the Ca coating shell, as shown in Figure 3(b,c). Thus, it is the Ca shell that would take part in any chemical activity.

Next we studied the interaction of a single hydrogen molecule with $C_{60}Ca_{32}$ by considering three different configurations as shown in Figure 4. In the top configuration (Figure 4(a)), H_2 is initially placed on top of a Ca atom with H−H and H−Ca distances set to 0.74 and 2.0 Å, respectively. Upon full optimization, the distance between H_2 and
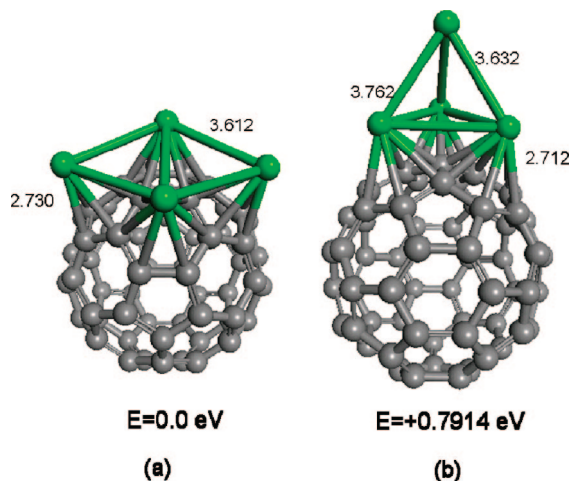
Figure 2. The optimized structures of Ca_4C_{60} with (a) the Ca atoms occupying the adjacent hollow sites and (b) the four forming a tetrahedron characteristic of a clustered configuration.

the Ca shell became 2.79 Å (Figure 4(b)). The hydrogen atoms remain molecularly bound, and the corresponding absorption energy is only 0.05 eV. In the bridge configuration (Figure 4(c)), H_2 was placed on the Ca−Ca bridge with initial H−H and H−Ca distances of 0.74 and 2.03 Å, respectively. However after optimization, the hydrogen molecule is found to dissociate and atomically bound at the centers of a Ca−Ca−Ca triangle with a binding energy of 0.74 eV/H (Figure 4(e)). This is much less than the binding energy in conventional metal hydrides. When H_2 is introduced on the hollow site of a Ca−Ca−Ca triangle (Figure 4(d)), the geometry also converged to that in Figure 4(e). Thus, in the preferred configuration, the hydrogen atoms bind dissociatively.

Now we consider an extreme situation, where all 60 triangles are occupied by H atoms. The optimized structure is given in Figure 5(a), where due to the insertion of H atoms, Ca−Ca and Ca−C distances have expanded to 3.75 and 2.86 Å, respectively, from the initial values of 3.68 and 2.75 Å. This increase in distance between fullerene-core and Ca-shell causes the C−C bond lengths to change from 1.465 and 1.446 Å to 1.447 and 1.425 Å, respectively. The binding energy of H atoms now reduces to 0.45 eV/H and is in the ideal thermodynamic range for the hydrogen storage materials' application in the mobile industry. With 60 H atoms bound to $C_{60}Ca_{32}$, the gravimetric density amounts to 3.0 wt %.

In Figure 5(b) we plot the charge distribution in the $C_{60}Ca_{32}H_{60}$ complex. Here yellow represents missing charge, and blue for charge gained. Due to further charge transfer from Ca to H, Ca sites become more positively charged. In fact, each Ca site carries a charge of +1.30 e, and each H site carries a charge of −0.535 e.

The significant positive charge on the Ca atoms allows the possibility that further hydrogen atoms may be bound to the $C_{60}Ca_{32}$ cluster. We note that Rao and Jena[31−33] had shown more than a decade ago that a positively charged atom can bind a large amount of hydrogen in quasi-molecular form through the charge polarization mechanism. To see if

$C_{60}Ca_{32}H_{60}$ can bind more hydrogen atoms we first carried out a model calculation. We began the analysis with a small model of Ca−C_2, as shown in Figure 6. When a Ca atom binds with C_2, 0.982 electrons are transferred to C atoms, and a H_2 is bound molecularly on top site of Ca with a binding of only 0.051 eV. The distance between the Ca and H atom is 2.881 Å (Figure 6(a)). This is very similar to the absorption of H_2 on the top site in $C_{60}Ca_{32}$ as discussed above. Now if we add a H atom next to Ca in the CaC_2 cluster the situation becomes very different. The charge transfer from Ca increases to +1.202e since the Ca atom now has to donate some charge to the H atom. The binding energy of H_2 to the $HCaC_2$ cluster increases to 0.171 eV, and correspondingly the distance between Ca and H decreases to 2.632 Å. The H−H bond also stretches from its molecular value of 0.74 Å to 0.757Å. These results suggest that the presence of H atoms next to Ca may allow $C_{60}Ca_{32}H_{60}$ to bind more hydrogen.

Following this clue, we added one H_2 molecule on top of each of the 32 Ca sites in $C_{60}Ca_{32}H_{60}$ and reoptimized the structure. The resulting geometry of the $C_{60}Ca_{32}H_{60}$-$32H_2$ complex is shown in Figure 7. The distance between H_2 and Ca shell is 2.621 Å, and the absorption energy of the second layer of hydrogen is 0.11 eV/H_2, similar to the values of the model system C_2CaH-H_2 described above. The total weight percentage of the complex $C_{60}Ca_{32}H_{60}$-$32H_2$ is now 6.2 wt %, providing hope that $C_{60}Ca_{32}$ may be a suitable material for hydrogen storage.

It is important to stress the advantages of a structure that derives stability from the geometric shell closure instead of electronic shell closure. For example, if the stability were of electronic origin, the cluster would have a large HOMO−LUMO gap, and as the size increases, this gap may close making the structure less stable. But for the geometric shell closure, there are no such limitations for the stability of a Ca coated higher fullerene. For example, in C_{60} there are 12 pentagons and 20 hexagons, as we have seen it can accommodate 32 Ca atoms in total. In C_{70}, there are 12 pentagons and 25 hexagons, so it should be able to accommodate 37 Ca atoms. Indeed, $Ca_{37}C_{70}$ has also been found to exhibit a conspicuous peak in the mass spectra[23] and hence is a magic cluster. We can use this "counting the rings of fullerenes"[23] as a means to determine the magic number of Ca atoms that can decorate a higher fullerene, and hence the maximum number of hydrogen it can hold. For example, we consider the C_{720} fullerene which has 12 pentagons and 350 hexagons and thus can accommodate 362 Ca atoms. These 362 Ca atoms again result in 720 triangular faces, in analogy with Figure 5(a), it can first bind 720 H atoms in dissociated form. Then the 362 Ca atoms can further bind 362 H_2 molecules in quasi-molecular form, thus forming a cluster with the composition $C_{720}Ca_{362}H_{720}$-$362H_2$ having a diameter of about 3.6 nm. The corresponding gravimetric density of hydrogen storage is 6.25%. It is only marginally larger than that in C_{60} fullerene. One can easily extend this rule to fullerenes of any size and determine the maximum hydrogen storing capacity of a Ca-coated fullerene system. Consider a fullerene with number of C atoms, N_C. The magic number, N_{Ca}, of Ca atoms it can accommodate is given by
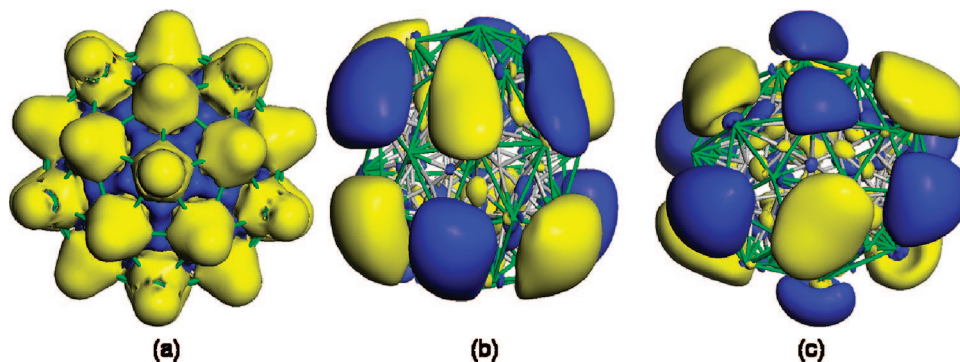
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Figure 3. (a) Charge difference and (b) HOMO and (c) LUMO of $C_{60}Ca_{32}$.
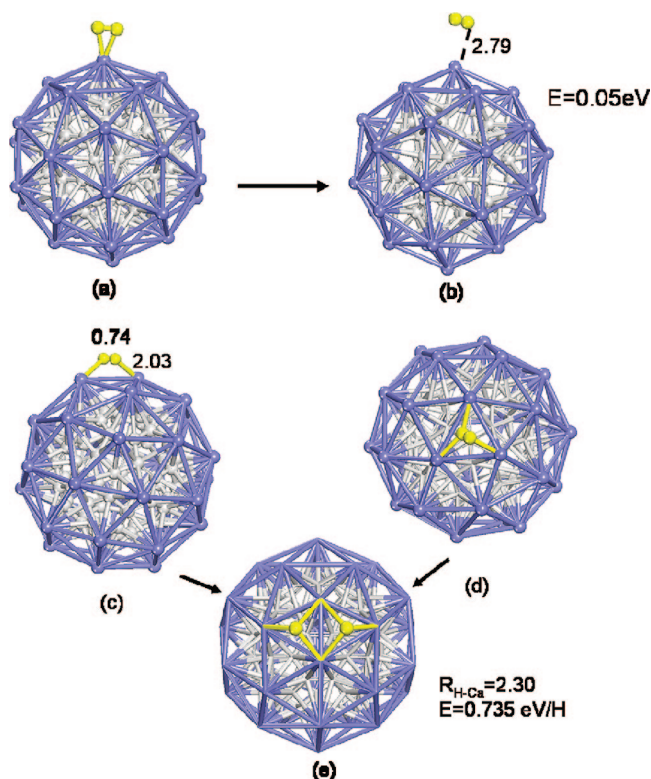

Figure 4. (a) Initial and (b) final geometry of H_2 placed at the on-top configuration. Initial geometries of H_2 placed on the (c) Ca–Ca bridge and (d) hollow site. The final optimized geometry in given in (e).
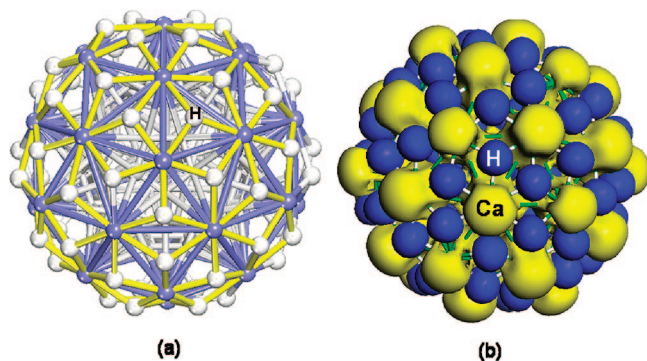

Figure 5. (a) Optimized geometry of and (b) charge distribution in $C_{60}Ca_{32}H_{60}$.

$N_{Ca} = N_C/2 + 2$. The metal-loading atomic percentage N_{Ca}/N_C is $(0.5 + 2/N_C) \times 100\%$. The total number, N_H, of stored
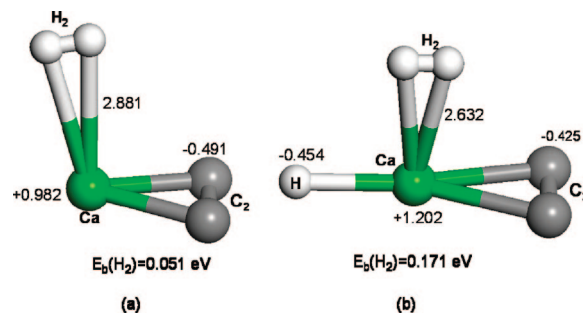

Figure 6. Model analysis of the effect of H insertion on the absorption of H_2.
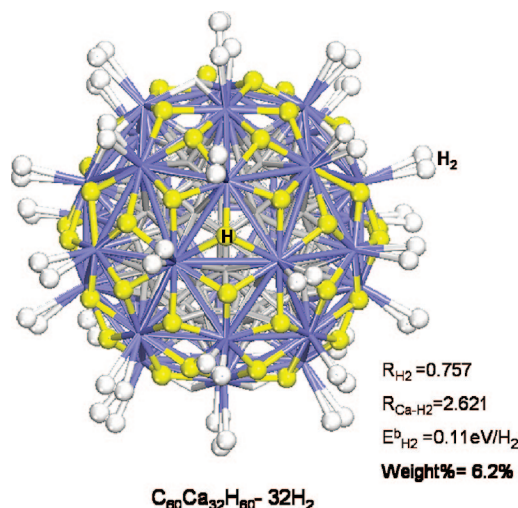

$C_{60}Ca_{32}H_{60}- 32H_2$

Figure 7. Geometry of 32 H_2 molecules absorbed on $C_{60}Ca_{32}H_{60}$.

hydrogen atoms in such a complex is then $N_C + 2N_{Ca}$. With this the hydrogen weight percentage W_H (%) can be calculated with following formula

$$WH(\%) = [(2N_c + 4) \times 1.0] \times 100\% / [N_c \times 12.0 + (0.5 \times N_c + 2) \times 40.0]$$

In Table 1, we give the changes of N_{ca}, N_H, A_{Ca}, and W_H with the size of fullerene. It is interesting to note that with the increase in fullerene size, the metal-loading atomic percentage decreases, saturating at 50% (Figure 8); while the weight percentage of stored hydrogen increases, terminating at 6.25% (Figure 9).

We also examined the possibility that $C_{60}Mg_{32}$ can store hydrogen with larger gravimetric density than $C_{60}Ca_{32}$ as Mg
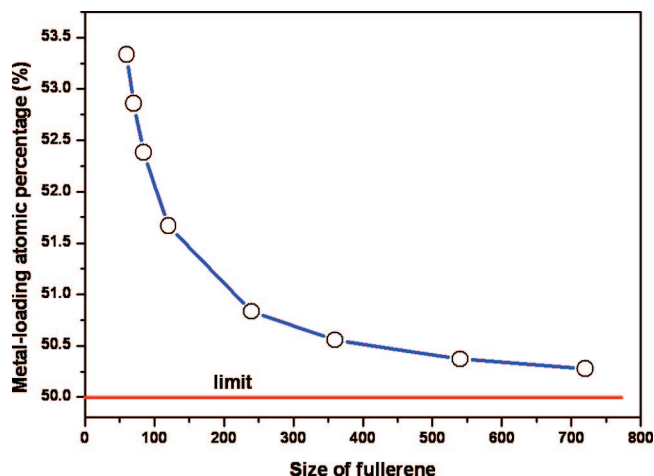
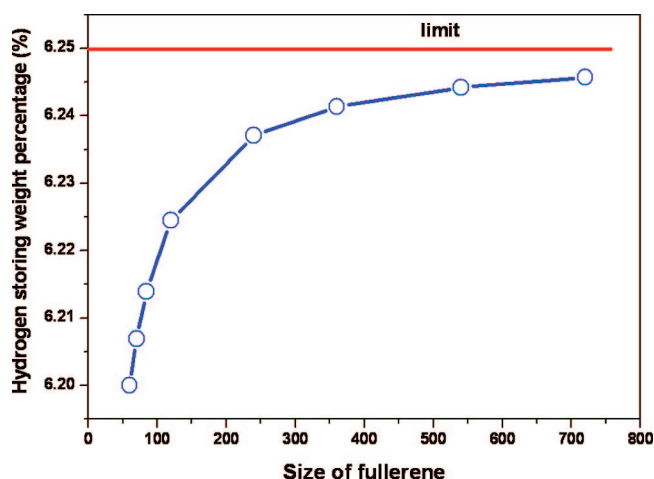**Figure 8.** Dependence of metal-loading atomic percentage with fullerene size.

Figure 9. Dependence of hydrogen gravimetric density with fullerene size.

Table 1. Fullerene Size (N_C), Number of Ca Atom (N_{Ca}), Total Number of Hydrogen (N_H), Metal-Loading Atomic Percentage (A_{Ca}), and Hydrogen Storage Weight Percentage (W_H)

N_c	N_{Ca}	N_H	A_{Ca} (%)	W_H (%)
60	32	124	53.3333	6.2000
72	37	144	52.8571	6.2069
84	44	172	52.3810	6.2139
120	62	244	51.6667	6.2245
240	122	484	50.8333	6.2371
360	182	724	50.5556	6.2414
540	272	1084	50.3704	6.2442
720	362	1444	50.2778	6.2457

belongs to the alkaline-earth series and is lighter than Ca. However only after 0.4 ps simulation, the structure is totally fractured as shown in Figure 1(c), indicating that due to the small size of Mg, 32 Mg atoms are not enough to cover the surface of C_{60}. We also studied the stability of $C_{60}Li_{32}$. Note that $C_{60}Li_{12}$ has been known to be a magic cluster, and decorating the remaining 20 hexagonal sites on C_{60} will lead to $C_{60}Li_{32}$. After 0.5 ps simulations, the initial Li coating layer ruptured, and Li atoms formed some small clusters dotted on the surface of C_{60} as shown in Figure 1(d).

In summary, we show that $C_{60}Ca_{32}$ is thermodynamically stable and can bind up to 6.2 wt % hydrogen with the first 3 wt % bound atomically with a reduced binding energy of 0.45 eV/H and the remaining 3.2 wt % quasi-molecularly with a binding energy of 0.11 eV/H_2. Our findings are different from the recent report,[34] where 92 H_2 molecules are stored corresponding to an uptake of 8.4 wt% with a binding energy of ∼0.4 eV/H_2 within LDA and ∼0.2 eV/H_2 within GGA. Furthermore, based on the fullerene counting rule,[23] we also show that as the fullerene size increases, the fully coated Ca fullerene cannot store more than 6.25 wt% hydrogen. Although Li and Mg are lighter in mass for a possible higher weight percentage of hydrogen storage, they cannot form stable and uniformly coated $M_{32}C_{60}$ structures as confirmed by our MD simulations.

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