Calcium as the Superior Coating Metal in Functionalization of Carbon Fullerenes for High-Capacity Hydrogen Storage

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(Received 6 December 2007; published 22 May 2008)

We explore theoretically the feasibility of functionalizing carbon nanostructures for hydrogen storage, focusing on the coating of C_{60} fullerenes with light alkaline-earth metals. Our first-principles density functional theory studies show that both Ca and Sr can bind strongly to the C_{60} surface, and highly prefer monolayer coating, thereby explaining existing experimental observations. The strong binding is attributed to an intriguing charge transfer mechanism involving the empty *d* levels of the metal elements. The charge redistribution, in turn, gives rise to electric fields surrounding the coated fullerenes, which can now function as ideal molecular hydrogen attractors. With a hydrogen uptake of >8.4 wt % on $Ca_{32}C_{60}$, Ca is superior to all the recently suggested metal coating elements.

DOI: 10.1103/PhysRevLett.100.206806 PACS numbers: 81.05.Tp, 68.43.−h, 73.22.−f, 84.60.Ve

Recent advances in materials science have witnessed a rapid expansion of research towards discoveries of novel materials for sustainable energy. In this cause, hydrogen has been viewed as a highly appealing energy carrier for renewable energy because of its abundance and environmental friendliness [1]. To achieve economic feasibility, hydrogen storage materials with high gravimetric and volumetric densities must be developed [2]. Furthermore, hydrogen recycling should be performed reversibly under near ambient conditions [3].

Carbon-based nanomaterials are widely studied for their application in hydrogen storage [4–8]. Pristine carbon nanostructures are chemically too inert to be useful for practical hydrogen storage [4]. One approach to increase their chemical activity is to substitutionally dope the nanostructures with light elements such as Be [5], but it has been difficult to experimentally realize it in a controlled way [9]; furthermore, the expected gravimetric density is very low, and Be is highly toxic [5]. Another is to coat the surfaces with transition [6,7] or alkali metals [10]. It is fundamentally difficult to achieve homogeneous monolayer coating using transition metal atoms [11,12]; furthermore, the resulted systems are too reactive, leading to partial dissociation of hydrogen molecule [7] and reduction of the total number of accessible hydrogen molecules. Whereas alkali atoms such as Li can be coated uniformly, the resulted systems would create too weak binding sites [13], prohibiting room temperature applications. A more recent study showed that charged fullerenes can bind hydrogen molecules strongly due to the polarization of H_2 by the charged fullerenes [14].

In this Letter, we use first-principles calculations within density functional theory (DFT) to explore the feasibility of functionalizing carbon nanostructures for hydrogen storage by coating C_{60} fullerenes with a different class of elements—light alkaline-earth metals (AEMs), the only elements between the too weak alkali and the too reactive transition metals. We show that, whereas Be and Mg can bind only weakly on C_{60}, Ca, and Sr can adsorb strongly, and also highly prefer monolayer coating. The strong binding for Ca and Sr is attributed to an intriguing charge transfer mechanism involving the empty *d* levels of the metals. The charge redistribution, in turn, gives rise to electric fields surrounding the coated fullerenes, which can now function as effective molecular hydrogen attractors. The resulting hydrogen uptake is >8.4 wt % on $Ca_{32}C_{60}$, making Ca the most attractive coating element among all the candidates considered so far in the literature (including the present work).

Our calculations were carried out using the Vienna *ab initio* simulation package (VASP) [15], with the exchange-correlation potential described by the Perdew-Wang version of the gradient generalized approximation (GGA) [16]. For selective cases, we also compared the GGA results with those from local density approximation (LDA) [17] described by Ceperley-Alder as parametrized by Perdew and Zunger [18]. We employed the projector-augmented wave (PAW) pseudopotentials [19]. The energy cutoff for the plane-wave basis set was 400 eV with the supercell size of 22 and 30 Å for MC_{60} (M = Be, Mg, Ca, and Sr) and $Ca_{32}C_{60}$, respectively. Our spin-polarized DFT calculations demonstrate that unlike transition metals, where spin components play an important role, the AEM elements show no spin polarization. All the considered structures were fully optimized with the force on each atom less than 0.01 eV/Å.

First, we consider the adsorption energetics of a single AEM atom onto C_{60}. We perform structure optimizations starting with possible metal adsorption sites on C_{60}. The metal-fullerene binding energy and the distance between the metal atom and C_{60} surface are calculated and compared with the results for Ti, which is one of the most widely studied coating metals [6,7]. We find significant differences in the binding behavior of different AEMs. Both Be and Mg bind to the fullerene very weakly via van der Waals interactions; their average binding energy is ~60 meV with an average distance of ~3.5 Å and their most preferred binding sites are located on top of a C_{60} single bond. In contrast, Ca and Sr are not stable when located near single bonds, but bind most strongly on top of a hexagonal ring with a binding strength of ~1.3 eV, which is roughly half of that of Ti. Such binding strengths are high enough to maintain stable configurations at room temperature, especially at higher AEM coverages [20].

Next, we address the underlying binding mechanism between AEMs and fullerenes. Figure 1 illustrates the partial density of states (PDOS) of the MC_{60} complexes ($M =$ Be, Mg, Ca, and Sr), where the metal atoms are located on top of a hexagonal ring and the PDOS of the metal atoms are threefold magnified. The highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of C_{60} are identified by their symmetries. In the case of Be and Mg coating, the metal atoms and fullerenes essentially preserve their individual DOS of the respective isolated states. The h_u and t_{1u} levels are rigidly shifted downward without level broadening. In particular, the s orbitals of Be and Mg show no indication of electron depletion. The high ionization potentials of Be and Mg [21] hinder the donation of metal valence s electrons to the fullerene. As a consequence, there is no charge transfer and no chemical bond formation between C_{60} and Be or Mg. We note that, given the van der Waals nature of the interaction, these conclusions for Be and Mg are valid and insensitive to their precise binding locations on C_{60}.

In contrast, fullerenes coated with Ca and Sr show completely different PDOS features, indicating strong hybridizations between the metal and carbon cage. In both cases fullerene related levels are shifted downward. More importantly, the states located near the Fermi level are strongly dispersed. The fullerene HOMO levels are split into doubly and triply degenerated states, while the LUMO levels spread over a wide range. In particular, the t_{1u} levels and the low-lying metal d orbitals become partially occupied. Also, strong hybridization between the carbon π and π^* orbitals and the metal d orbitals can be observed. At the same time, a complete depletion of metal s orbitals occurs, indicating two electrons have transferred from the metal to C_{60}.

It turns out that Ca and Sr bind to C_{60} through a very unique mechanism. Unlike Be and Mg, Ca and Sr have available empty d orbitals, which results in a significant difference in their chemical activities as they are attached to the fullerene. It is much easier for Ca and Sr to donate their s electrons to the fullerene due to their relatively low ionization potentials [21]. The donated electrons partially fill the fullerene π^* orbitals as indicated by their PDOSs. More importantly, as Ca and Sr atoms are brought close to the C_{60} cage, their empty d orbitals split under the strong ligand field generated by the fullerene. There is a finite probability for C_{60} to back donate part of its received electrons from the metal atom to the low-lying d orbitals, resulting in a strong hybridization between the π and d orbitals and partial occupancy of d. This electron donation/back-donation mechanism helps considerably to stabilize the chemical interaction between C_{60} and Ca or Sr atoms.

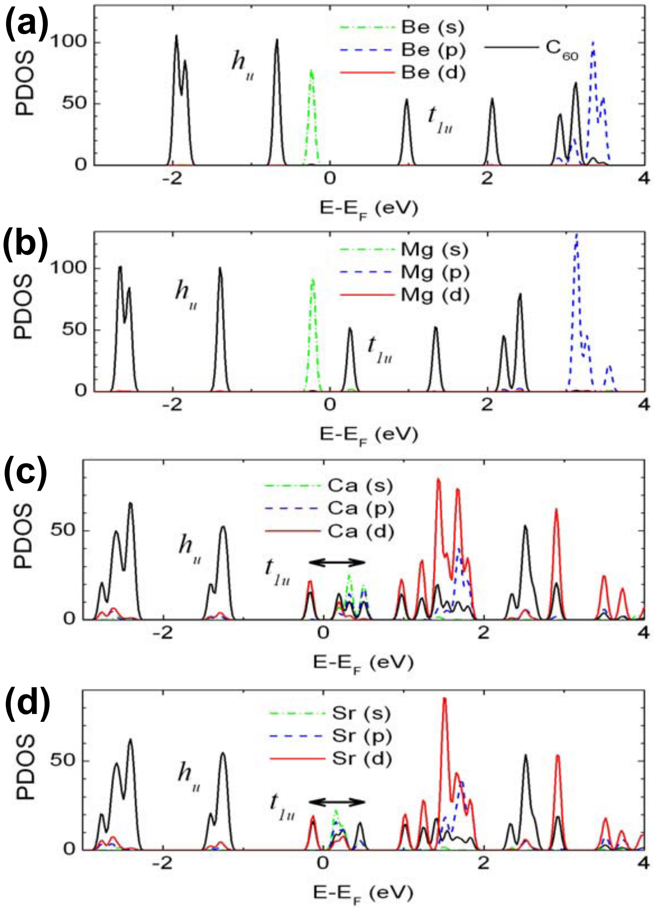
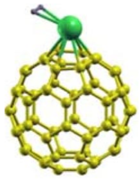
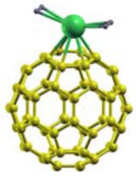
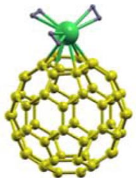
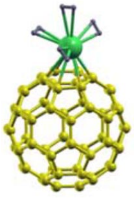
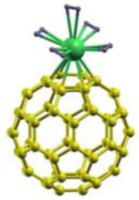


FIG. 1 (color online). Partial density of states (PDOS in arbitrary units) of MC_{60} complexes ($M =$ Be, Mg, Ca, and Sr), where the metal atoms are located on top of a hexagonal ring. Here, the PDOS of the metal atoms are displayed in threefold magnification. In all panels, the solid black lines denote the total PDOS of the 60 C atoms (C_{60}).

Since Be and Mg cannot be stabilized on C_{60}, we only consider Ca and Sr as potential coating elements. Earlier experimental data from mass spectrum measurements showed that C_{60} can be evenly covered by 32 AEM (AEM = Ca, Sr, and Ba) atoms, strongly suggesting that all the 32 faces of pentagon and hexagon sites on C_{60} are occupied [22]. Previous theoretical studies of the systems [20] also supported strong binding of Ca on C_{60}. Here, we have compared the relative stability of competing structural configurations consisting of 12 Ca atoms on C_{60}, including a homogeneous occupation of the 12 fullerene pentagons (0D), a 2-dimensional (2D) closed-packed layer, and a 3D icosahedral cluster [12], and find that the 2D structure is more stable than the 3D cluster by 0.7 eV, while

TABLE I. Hydrogen binding energies (in eV) for MC_{60} ($M = $ Ca, Sr). For Ca, the GGA and LDA results are also compared.

					
Ca	0.222	0.214	0.233	0.206	0.204
(LDA)	0.413	0.396	0.415	0.376	0.385
Sr	0.200	0.192	0.202	0.181	0.179

the 0D configuration is less stable than the 3D cluster by 4.8 eV. This conclusion is qualitatively different from that of Ti coating, where 3D clustering is always favored energetically [12].

Now we investigate the interaction between these organometallic complexes with hydrogen molecules. We find that Ca or Sr coating results in strong molecular hydrogen binding sites. On the other hand, Be and Mg atoms bind H_2 very weakly, with a binding strength reflecting typical van der Waals interactions. The hydrogen binding energies (E_b) for MC_{60} ($M =$ Ca, Sr) are summarized in Table I, showing the GGA results for both metals and the LDA results for Ca, where $E_b = [E(MC_{60}) + N \times E(H_2) - E(NH_2 - MC_{60})]/N$. Step by step, we add additional hydrogen molecules close to the metal atom, where the NH_2-MC_{60} complex with N hydrogen molecules ($N = 1, \ldots, 5$) is fully optimized. Surprisingly, a single Ca or Sr atom can adsorb up to 5 H_2 molecules with a relatively constant binding energy. Electrons in the fullerene undergo major changes in their charge distribution upon Ca and Sr coating and the transferred charges are spread over due to the diffusive nature of the d orbitals [see Figs. 1(c) and 1(d)]. The significant charge redistribution results in an electric field, which is strong enough to attract up to 5 H_2 molecules with a uniform binding energy of ~0.2 eV per H_2 according to GGA and ~0.4 eV per H_2 if LDA is employed. It is known that GGA underestimates the binding strength, while LDA results in too high values [5,23]. The optimized structures show that none of the relevant physical quantities, such as the average H_2 binding energy, the bond length between H_2 and the metal atom, and the H-H distance, undergo significant changes as the number of H_2 molecules increases. In contrast, for the case of coating with transition metals, the H_2 binding strength sensitively varies with the number of attached H_2 molecules, as signified by the dissociation of the first hydrogen molecule where the binding is too strong [7].

The underlying binding mechanism of H_2 on Ca- or Sr-coated fullerenes is qualitatively different from that of H_2 on transition-metal-coated complexes [7]. In the middle panel of Fig. 2 we compare the spin-resolved PDOS of a single hydrogen molecule adsorbed on Ca- or Ti-coated fullerene. The most stable configurations are displayed in the left panel. Hydrogen is adsorbed to Ti in atomic form with a gain of 1.04 eV per H_2. In the case of Ca, molecular hydrogen attachment to the side of Ca occurs with a 0.2 eV energy gain per molecule. Transition metals bind hydrogen through the Dewar interaction [24] as highlighted in Fig. 2(a), where a hydrogen molecule transfers its σ electrons to the Ti d orbitals, while the metal back-donates electrons to the hydrogen σ^* orbitals. This process naturally reduces the number of accessible hydrogen molecules in transition-metal-coated systems. In the case of Ca-doped fullerenes, however, the hydrogen σ orbital located far below the Fermi level remains intact [see Fig. 2(b)]. We further analyze charge density differences ($\Delta\rho$) from which the charge density variations induced by hydrogen adsorption is measured. The right panel of Fig. 2 shows the isosurfaces of charge density differences, where the red (or gray) and blue (or dark gray) colors represent electron accumulation and depletion regions, respectively. Electrons transferred from Ti are accumulated to the hydrogen atoms, while polarization of the hydrogen molecule occurs near the Ca atom. This clearly indicates that the hydrogen binding to Ca is originated from its polarization under the

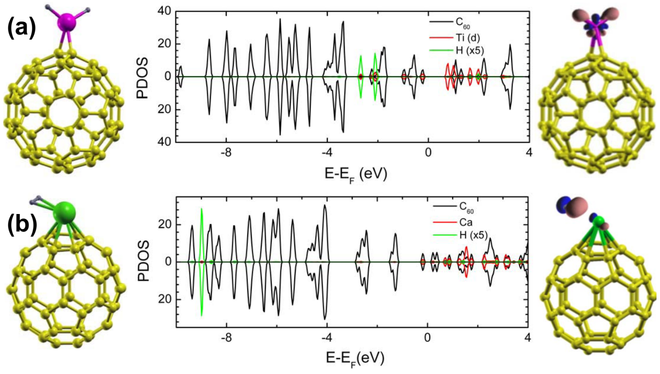


FIG. 2 (color online). Spin-resolved PDOS (in arbitrary units) of a single hydrogen molecule adsorbed on Ti-coated (a) and Ca-coated (b) fullerenes. For Ti, only its d levels are plotted, and the hydrogen states are fivefold magnified. The isosurfaces of charge density differences ($\Delta\rho$) are shown in the right panel. The $\Delta\rho$ is chosen to be $\pm 0.2\ e/\text{Å}^3$ for (a) and $\pm 0.02\ e/\text{Å}^3$ for (b), respectively.

electric field produced by the Ca atom, rather than via the Dewar mechanism.

Because Ca and Sr have comparable hydrogen binding strength, and both are stable against clustering, we will only focus on fully Ca-coated fullerenes having higher gravimetric density. For structure optimization of $Ca_{32}C_{60}$, we choose an initial geometry where a Ca atom is located above the center of each pentagon or hexagon. The fully relaxed structure of $Ca_{32}C_{60}$ is shown in Fig. 3(a). We then calculate the charge density differences ($\Delta\rho$) of $Ca_{32}C_{60}$, which measure the charge density variations of $Ca_{32}C_{60}$ induced by the adsorption of 32 Ca atoms onto a C_{60} cage. Figure 3(a) shows the isosurface ($\Delta\rho = \pm 0.04\ e/\text{Å}^3$) of charge density differences. The substantial charge redistribution upon Ca coating leads to a high electric field near the Ca atoms. Figure 3(b) shows the radial component of the electric field from the center of the carbon cage to one of the Ca adatoms. At the optimum hydrogen distance (marked by the gray shaded region), the electric field associated with the charge redistribution reaches up to $\sim 2.4 \times 10^{10}$ V/m, which is high enough to significantly polarize the H_2 molecules [14]. Finally, we introduce a total of 92 hydrogen molecules onto the surface of the $Ca_{32}C_{60}$ complex system. The fully optimized geometry is shown in Fig. 3(c), corresponding to a hydrogen 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. We note that this hydrogen uptake is a lower bound of the gravimetric capacity, as it is conceivable that more hydrogen molecules are likely to be accommodated onto the system.

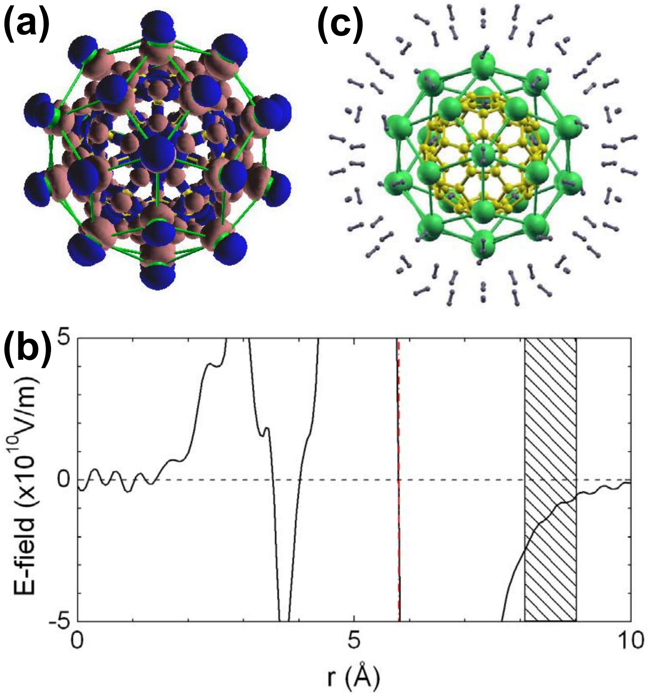


FIG. 3 (color online). Hydrogen interaction with $Ca_{32}C_{60}$. (a) The isosurface ($\Delta\rho = \pm 0.04\ e/\text{Å}^3$) of charge density differences caused upon adsorption of the 32 Ca atoms onto the carbon cage. (b) The radial component of the electric field associated with the structure shown in (a). The dashed red (or gray) line denotes the Ca location. (c) The optimized hydrogen-organometallic complex of $92H_2$-$Ca_{32}C_{60}$ with a hydrogen uptake of 8.4 wt %.

In summary, our first-principles studies have identified Ca as the most desirable coating metal element for functionalizing carbon fullerenes into high-capacity hydrogen storage media. This strong prediction is expected to be also applicable to other related low-dimensional systems, and to motivate an active line of experimental efforts.

This work was supported by DOE (Grant No. DE-FG02-03ER46091, the Division of Materials Sciences and Engineering, and the Hydrogen Sorption Center of Excellence) and in part by the Chinese Academy of Sciences and U.S. NSF (Grant No. DMR-0606485). The calculations were performed at DOE's NERSC.

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