Calcium-decorated carbon nanotubes for high-capacity hydrogen storage: First-principles calculations

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Using first-principles calculations, we perform a search for high-capacity hydrogen storage media based on individually dispersed calcium atoms on doped or defective carbon nanotubes. We find that up to six H_2 molecules can bind to a Ca atom each with a desirable binding energy of ~ 0.2 eV/H_2. The hybridization of the empty Ca $3d$ orbitals with the H_2 σ orbitals contributes to the H_2 binding, and Ca clustering is suppressed by preferential binding of Ca atoms to doped boron and defect sites dispersed on carbon nanotubes. We also show that individual Ca-decorated B-doped CNTs with a concentration of ~ 6 at. % B doping can reach the gravimetric capacity of ~ 5 wt. % hydrogen.

I. INTRODUCTION

Hydrogen storage at appropriate density in solid-state materials can be an essential requirement for the development of hydrogen fuel-cell powered vehicles. However, feasible candidate materials are scarce.[1,2] Suggestions for hydrogen storage in carbon nanotubes (CNTs) and other nanostructured materials have been made because of the possibility of reversibility, fast kinetics, and high capacity (large surface area).[3] Many of the experimental studies were done on pristine organic materials and metal-organic frameworks;[3–6] however, it has been found that the hydrogen storage capacity in these systems greatly diminishes at room temperature and ambient pressure.[6,7] This is attributed to the weak interaction between hydrogen molecules and the materials by physisorption (~ 0.04 eV).[7] More recent theoretical studies have been devoted to finding and designing materials which enhance the interactions to the desirable binding energy of 0.2–0.6 eV.[8–17]

In recent years, studies of early transition-metal (i.e., Sc, Ti, and V) decorated carbon nanotubes, fullerenes, and polymers have attracted much attention as possible systems for hydrogen storage applications at room temperature and ambient pressure.[13–15] It was expected that these materials not only enhance the interaction between the transition-metal element and H_2, up to $\sim 0.2-0.6$ eV via the Kubas interaction (hybridization of the d states with the H_2 states),[18] but also meet the U.S. Department of Energy (DOE) goal of obtaining a gravimetric capacity of 9 wt. % by the year 2015.[19] Recently, the experimental groups of Antonelli *et al.*[20] and Shivaram and Phillips[21] showed progress in enhancing the interaction of H_2 in reducible mesoporous Ti oxides and Ti-ethylene complexes, which are, unfortunately, still short of the needed interaction in the theoretically suggested structures for room-temperature hydrogen storage. Another issue is that, based on energy consideration, transition-metal atoms generally prefer being clustered to being individually dispersed on nanomaterials because of their large cohesive energy (i.e., ~ 4 eV). Clustering changes significantly the adsorption nature of the H_2 molecules,[22,23] and this is a major

challenge when trying to produce metal-decorated hydrogen storage nanomaterials.

Recently, Yoon *et al.*[24] suggested another material system, calcium-monolayer-coated fullerenes, for high-capacity hydrogen storage. The motivating idea is that H_2 molecules adsorb more strongly on Ca-coated fullerenes than on bare fullerenes because of the polarization of the H_2 molecules induced by the electric field produced by the Ca atoms. The charge transfer of the two $4s$ electrons to the fullerenes causes the fullerenes to appear charged.[25] Calcium-coated C_{60} ($Ca_{32}C_{60}$) is calculated to uptake as many as 92 H_2 molecules (2.7 H_2 per Ca) with a maximum storage capacity that can reach 8.4 wt. %.

Here, instead of considering monolayer Ca-coated fullerenes, we study the case of individual Ca atoms dispersed on carbon nanotubes. Different physical mechanisms from those in Ref. 24 are employed. We use Ca as in the transition-metal atoms as attractors of H_2 molecules, so that the number of adsorbed H_2 molecules per Ca is increased via the Kubas interaction. Furthermore, since the cohesive energy of calcium (1.84 eV) is much smaller than that of the transition metals (~ 4 eV), we expect that the clustering problems in metal-decorated nanostructured materials might be overcome by calcium.

To achieve our goal, we conduct a systematic search for high-capacity hydrogen storage media consisting of individual calcium atoms decorated on doped or defective carbon nanotubes. We find that up to six H_2 molecules are attached per Ca with a binding energy of ~ 0.2 eV/H_2 and that the hybridization of the empty Ca $3d$ orbitals with the H_2 σ orbitals contributes to the H_2 adsorption. Our calculations show that the Ca atoms may be individually dispersed on B-doped and defective carbon nanotubes without Ca clustering. We also show that the hydrogen storage capacity can reach 5 wt. % on 6 at. % B-doped CNTs.

II. COMPUTATIONAL DETAILS

All our calculations were carried out using a first-principles method based on density functional theory as

TABLE I. Calculated binding energy of Ca (eV/Ca) and H_2 molecules (eV/H_2) for an isolated Ca atom decorated on a pristine (7,7) CNT and on a nitrogen-dopant, a boron-dopant, a Stone Wales-defect, a mono-vacancy, and a di-vacancy on a (7,7) CNT, respectively, as a function of the number of adsorbed H_2 molecules.

	Ca	1 H_2	2 H_2	3 H_2	4 H_2	5 H_2	6 H_2
CNT	0.88	0.21	0.21	0.21	0.21	0.19	0.17
N-CNT	0.61	0.23	0.22	0.21	0.21	0.19	
B-CNT	1.82	0.20	0.21	0.20	0.19	0.18	
SW-CNT	2.15	0.16	0.17	0.16	0.14	0.13	
MV-CNT	3.30	0.16	0.16	0.14	0.13	0.12	
DV-CNT	2.20	0.20	0.19	0.17	0.16	0.15	

implemented in the Vienna *ab initio* simulation package (VASP) with a projector-augmented-wave (PAW) basis set.[26,27] The exchange-correlation energy functional of Perdew and Wang in the generalized gradient approximation (GGA) was used,[28] and the kinetic energy cutoff was taken to be 26 Ry. The optimized atomic positions were obtained by relaxation until the Hellmann-Feynman force on each atom was less than 0.01 eV/Å. Supercell calculations were employed throughout where the carbon atoms on adjacent nanotubes are separated by over 10 Å.

III. RESULTS AND DISCUSSION

To search for high-capacity hydrogen-storage nanostructures consisting of combination of carbon nanotubes and calcium, we first consider a pristine (7,7) CNT and the case of nitrogen substitutional doping, boron substitutional doping, Stone Wales (SW) defect, mono-vacancy (MV), and di-vacancy (DV) on a (7,7) CNT to examine the local structure of the Ca attachment. A single calcium atom is attached to each of the above six structures, and the calculated binding energies of Ca are presented in Table I. We then calculate the binding energy of H_2 molecules on Ca in these six structures as a function of the number of H_2 molecules adsorbed. Figure 1 shows the optimized geometries for the configuration with maximally adsorbed number of H_2 molecules on a single Ca atom for the six structures considered. The calculated binding energies of the H_2 molecules using the GGA are also presented in Table I. As in previous studies of binding energies of weak bonds, the calculated values with the local density approximation (LDA) are approximately twice as much as those with the GGA, and the correct values are expected to be somewhere in between the two approximations. Up to five (or six) H_2 molecules are adsorbed on a Ca atom, and the distance between the Ca atom and the H_2 molecule is ~2.45 Å. The bond length of H_2 is slightly elongated from 0.75 Å of the isolated molecule to ~0.77 Å.

We investigate whether in the present case the unoccupied Ca 3d levels might contribute to the adsorption of the H_2 molecules via the hybridization of the d states with the H_2 states as in the case of H_2 binding to transition-metal atoms.[18] Figures 2(a) and 2(b) display the projected density of states (PDOS) for the H_2 molecules and the Ca d orbitals when four H_2 molecules are adsorbed on a Ca attached on a

pristine and *B*-doped CNTs, respectively. Hybridization of the Ca 3d orbitals with the H_2 σ state at ~−9 eV, and hybridization of the Ca 3d orbitals with the H_2 σ^* orbitals at ~−0.1 eV are seen in Fig. 2(a). Similar results are obtained for the hybridization of the Ca 3d states with the H_2 σ and σ^* orbitals in *B*-doped CNT as shown in Fig. 2(b). These hybridizations are analogous to those found in H_2 adsorption on transition-metal atoms in the literature.[13,14] For comparison, we show in Fig. 2(c) the PDOS for the H_2 molecules and scandium (Sc) when four H_2 molecules are adsorbed on a Sc atom attached onto a CNT (with a binding energy of 0.51 eV/H_2). It has been shown theoretically that the binding mechanism of H_2 to transition metals arises basically from the hybridization of the d levels with the H_2 states.[13] In
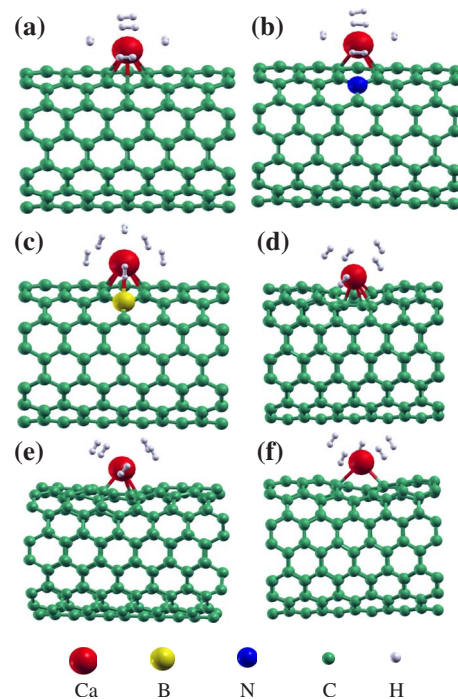

FIG. 1. (Color online) Optimized atomic geometries of Ca-decorated CNTs with maximum number of H_2 molecules attached to the Ca atom. (a)–(f) show the geometries for maximally adsorbed H_2 molecules to a Ca atom attached to a pristine (7,7) CNT and to a (7,7) CNT with a single *N* dopant, a single *B* dopant, a Stone-Wales defect, a mono-vacancy, and a di-vacancy, respectively.
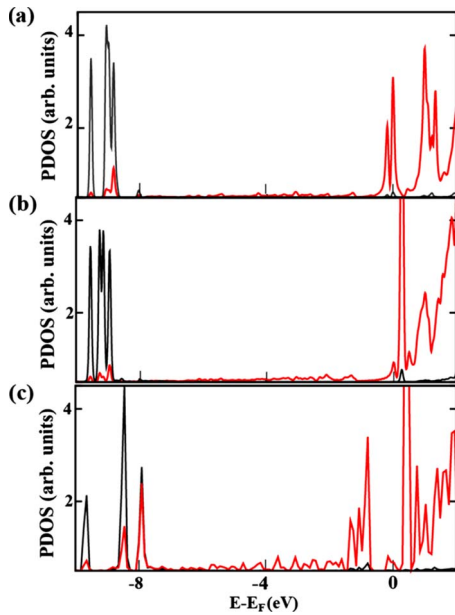
FIG. 2. (Color online) PDOS of the Ca (Sc) $3d$ orbitals and H_2 σ orbitals involved in the adsorption of four H_2 molecules on (a) Ca-decorated pristine, (b) Ca-decorated B-doped, and (c) Sc-decorated pristine (7,7) CNTs. The red (dark gray) line is the PDOS of the Ca or Sc $3d$ (H_2) states. The Fermi level is set to zero.

Fig. 2(c), the peaks center around -10 to -8 eV correspond to the hybridization of the Sc $3d$ with the H_2 σ orbitals, and the peaks center around -2 to 0 eV correspond to the hybridization of the Sc $3d$ with the H_2 σ^* orbitals, which is the same as the Ca case above except for a smaller strength. These hybridizations were not considered in the interpretation of the results in the Yoon *et al.*[24] paper in which the binding mechanism of H_2 molecules is attributed to the induced polarization of the H_2 molecules by the Ca attached on fullerenes. We paid attention to the fact that the binding energy of the H_2 molecules on Ca-decorated C_{60} (Ref. 24) and Li-decorated B_{80} (Ref. 29) is ~ 0.2 and ~ 0.1 eV/H_2, respectively, although the electric field at the position of the H_2 molecule is the same ($\sim 2 \times 10^{10}$ V/m) in both cases. Therefore, our analysis shows that the hybridization of the Ca $3d$ states with the H_2 σ orbitals and the polarization of the H_2 molecules both contribute to the H_2 adsorption on Ca.

We now address the important issue of metal adsorbate clustering. Our calculations show that Ca clustering takes place on pristine and N-doped CNTs because of the small binding energy of Ca to the CNTs (0.88 and 0.61 eV, respectively). Figures 3(a) and 3(b) show the optimized geometries for two aggregated Ca and for individually isolated Ca on pristine CNT where the aggregated case is energetically lower by 0.98 eV (per 2 Ca atoms) as compared with the isolated case. Figure 3(c) shows seven H_2 molecules put on the aggregated Ca with a distance of ~ 2 Å between the H_2 molecules and the Ca before energy minimization is performed. The aggregation of Ca results in the dissociation of one H_2 molecule as displayed in Fig. 3(d), and therefore the number of adsorbed H_2 molecules as well as the binding energy of the H_2 molecules are reduced. This behavior is
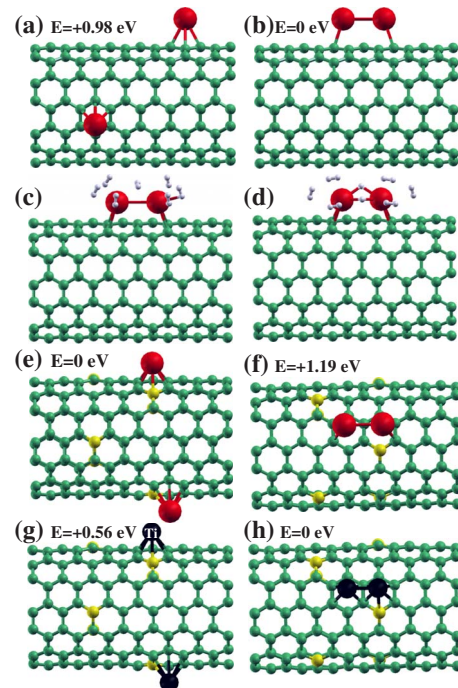

FIG. 3. (Color online) (a) Two Ca atoms individually attached on a (7,7) pristine CNT. (b) Two Ca atoms aggregated on a pristine (7,7) CNT. (c) Initial geometry of seven H_2 molecules on the two aggregated Ca atoms. (d) Geometry of the seven H_2 molecules on the two aggregated Ca obtained from energy minimization calculation. (e) Two Ca atoms individually attached on a B-doped (7,7) CNT. (f) Two Ca atoms aggregated on a B-doped (7,7) CNT. (g) Two Ti atoms individually attached on a B-doped (7,7) CNT. (h) Two Ti atoms aggregated on a B-doped (7,7) CNT. The total energy of the lower energy structure between aggregated and unaggregated structures is set to zero.

similar to clustering effects of transition metals on other nanomaterials.[22,23] In contrast, when two Ca atoms are individually dispersed on a B-doped CNT, the energy is 1.19 eV (per 2 Ca atoms) lower than the aggregated case as shown in Figs. 3(e) and 3(f). We also confirmed that, isolated Ca atoms attached to defects on CNTs with SW, MV, and DV defects are energetically preferred over the aggregated case by 0.92, 1.70, and 0.82 eV (per 2 Ca atoms), respectively. This is ascribed to a significantly larger binding energy of Ca to the defect site than the calculated-Ca dimer energy (~ 0.3 eV/Ca in vacuum). We find that the binding energy of Ca near the B site on a B-doped CNT monotonously increases as the B concentration increases. At 3 at. % B doping concentration, the binding energy of Ca reaches 3.2 eV which is much larger than the calculated cohesive energy of bulk Ca, 1.87 eV (1.84 eV experimental value). The enhancement of binding was observed in calculations for transition metals on B-doped fullerenes and graphene as well.[13,30] Therefore Ca can be individually dispersed on CNTs with B doping, SW defect, and vacancies. B-doped CNTs among CNTs with B dopants, SW, MV, and DV are the best for hydrogen storage purposes because the number of adsorbed H_2 molecules per Ca is the largest. On the other hand, the aggregation of titanium atoms (we chose Ti among other TMs because Ti is the best TM element for hydrogen
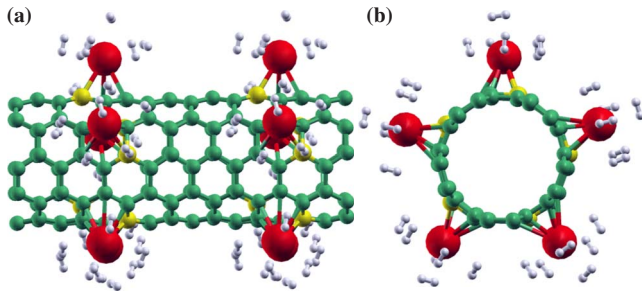
FIG. 4. (Color online) (a) and (b) show the side view and cross-sectional view for the optimized atomic structure of maximal number of adsorbed H_2 molecules for a *B*-doped (5,5) CNT (6.25 at. % of *B*), respectively.

storage purposes)[15] is still favorable for *B*-doped CNT as shown in Figs. 3(g) and 3(h) even if the binding energy of the Ti atom is enhanced by 3.4 eV per Ti atom as compared to that (2.2 eV per Ti atom) on pristine CNT. This nonaggregation feature of Ca should make it more effective in binding H_2 than the transition-metal elements proposed previously in the literature.[12–14] We have also calculated the binding energy of Ca in several well-known organic molecules to explore the tendency toward Ca dispersion. The values for the binding energy are 1.30, 0.16, and 0.63 eV per atom for Ca on fullerene (C_{60}), benzene, and *trans*-polyacetylene, respectively. Thus, for pristine organic materials, individual dispersion of Ca atoms is difficult in view of the large bulk cohesive energy of Ca.

We have investigated the effects of nanotube chiral index (metallic vs semiconducting) and curvature of *B*-doped CNTs on Ca and H_2 adsorption. On a *B*-doped (11,0) CNT [which is close to the diameter of a (7,7) CNT], the calculated binding energy of Ca is 1.88 eV and the binding energy of H_2 molecules are 0.18, 0.17, 0.19, 0.17, 0.16, and 0.15 eV/H_2 for 1, 2, 3, 4, 5, and 6 H_2 molecules on Ca, respectively, which are almost the same as those on *B*-doped (7,7) CNT. These results indicate that the binding energy of Ca or H_2 has little to do with the chirality of the CNTs. We checked the curvature effects of CNTs on the binding energy of Ca as well. The binding energy of the Ca atom is calculated to be 1.84, 1.74, and 1.67 eV on *B*-doped (6,6), (5,5), and (4,4) CNTs, respectively. Therefore, any indexes of CNTs can be used as backbones. We also found that the dopant *B* atoms and defects we considered prefer being dispersed as opposed to being clustered on carbon nanotubes. Figure 4 shows the fully optimized structure for a maximum hydrogen-storage capacity in (5,5) CNT with a concentration of 6.25 at. % *B*, corresponding to 4.94 wt. % uptake of H_2 molecules where the molecular formula may be expressed as $(C_{75}B_5 \cdot 5Ca \cdot 30H_2)_n$ (*n* is an integer). The volumetric hydrogen density is ~30 kg/m^3 when the CNTs with adsorbed H_2 molecules are packed by the distance of 3.6 Å.

Our results hence demonstrate the potential of Ca-decorated carbon nanotubes with *B* doping or other defects

as a hydrogen storage medium. It has been experimentally observed that *B* doping concentration in carbon nanotubes can be up to 15 at. % (Ref. 31) and that topological defects such as the Stone-Wales defect and mono- and di-vacancies in carbon nanotubes can be created by ion irradiation for various applications as well.[32] These experimental observations show that the Ca-decorated *B*-doped or defective CNTs we propose here can be synthesized using current technology. Another attractive feature is that Ca is the fifth most abundant element in the earth's crust. For practical storage applications, although a considerable amount of Ca is needed, there should be ample supply. We have also considered the stability of H_2 binding on Ca atoms dispersed CNTs with respect to the formation of bulk CaH_2. The configuration of six H_2 molecules adsorbed on the Ca-decorated mono-vacancy CNTs is energetically lower than that of bulk CaH_2 by 0.86 eV/Ca. In other cases, the energy of H_2 molecules binding on Ca-decorated CNTs is higher than the formation of bulk CaH_2; however, we think that the structures for Ca-decorated *B*-doped, Stone Wales-defected, and di-vacancy CNTs are still stable because the activation barriers between H_2 binding on Ca-decorated CNTs and the formation of bulk CaH_2 are higher than ~1.2 eV/Ca, much higher than the desorption temperature in our system (approximately 60 °C).

IV. CONCLUSION

In conclusion, we have demonstrated the possibility that individually dispersed Ca-decorated carbon nanotubes can serve as a high-capacity hydrogen storage medium. The empty *d* states of Ca provide an added mechanism for H_2 attachment as in transition-metal elements. However, unlike the transition-metal elements, Ca has a much lower tendency for clustering on doped or defective CNTs. We feel that these systems can be made, and we encourage an experimental search to synthesize these hydrogen storage nanomaterials that may operate at room temperature and ambient pressure.

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