

Stable calcium adsorbates on carbon nanostructures: Applications for high-capacity hydrogen storage

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We have investigated the stability of calcium adsorbates on carbon nanotubes and defective graphene using first-principles calculations. For ultranarrow carbon nanotubes, we find that the effect of chirality is more important to the adsorption as compared to the diameter (D). The binding energy for a calcium atom absorbed on the (5,0) tube is about 1.4 eV higher than that on the (3,3) tube. We also find that calcium atoms on the octagon defect of graphene are also stable. The binding energies of calcium adsorbates on narrow tubes ($3.2 \text{ \AA} < D < 5.6 \text{ \AA}$) and defective graphene are high, which indicates that the calcium monolayer should be stable without clustering. The results show that every calcium atom can uptake four to five H_2 and the hydrogen storage can reach 9 wt %.

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I. INTRODUCTION

Hydrogen is an ideal energy resource for its high efficiency and environmental friendliness.¹ The safe and compact storage of hydrogen is important for the applications. Various carbon-based nanomaterials have been intensively investigated as hydrogen storage medium. Hydrogen molecule physisorption on carbon nanotubes is rather weak with high energy barrier for H_2 dissociation on the pristine tubes² and hydrogen storage requires high pressure and very low temperature.^{3,4} It is reported that 65 ± 15 at. % atomic hydrogenation of carbon atoms can be achieved on carbon nanotubes with moderate diameters.^{5,6} However, the maximum of hydrogen storage is only 7.7 wt % even carbon nanotubes are fully hydrogenated.

Metal dispersed carbon nanostructures have been approved to be more efficient for hydrogen storage. A single transition-metal atom (Sc, Ti, and Ni) coated on C_{60} or carbon nanotube surface can bind up three to five H_2 .⁷⁻¹⁰ Thus, the dispersed C_{60} and nanotubes can adsorb up to 6.8–10 wt % hydrogen with high metal coverage. Carbon nanomaterials coated with alkali and alkaline-earth atoms can also be used for hydrogen storage. Intercalated alkali atoms in carbon nanotubes would significantly enhance the hydrogen storage.¹¹ The isolated clusters ($\text{Li}_{12}\text{C}_{60}$, Na_8C_{60} , and $\text{Ca}_{32}\text{C}_{60}$) where metal atoms are capped onto the pentagonal and hexagonal faces of C_{60} are stable, which can store H_2 up to 8.4–9.5 wt %.¹²⁻¹⁴ The charge transfer from metal atoms to C_{60} gives rise to the electric field surrounding the coated fullerenes and enhances the H_2 adsorption. Similarly, charged fullerenes can gain storage capacities of up to 8.0 wt %.¹⁵

Metal monolayer coated on carbon nanomaterials is important for hydrogen storage medium. However, clustering of Ti atoms¹⁶ on C_{60} surface is energetically preferable, which greatly reduces the weight percentage of hydrogen storage. Similar problems could exist in the metal dispersed carbon nanotubes. In fact, metal atoms tend to form clusters on the

surface of carbon nanomaterials if the binding energies are much lower than that of bulk structures. It is important to find the stable adsorbates without clustering tendency on the carbon nanomaterials. In this paper, we have investigated calcium coated carbon nanotubes and defective graphene using first-principles calculations. We focus on how the surface configuration affects the adsorption stability. It is shown that Ca adsorbate on narrow ($n, 0$) carbon nanotubes and defective graphene are stable and the hydrogen uptake on Ca dispersed carbon nanomaterials can be achieved to 9 wt %.

II. METHODS

Our calculations are performed using Vienna *Ab initio* Simulation Package (VASP).¹⁷ The approach is based on the density-functional theory in a plane-wave basis set with the Vanderbilt ultrasoft pseudopotentials.¹⁸ We use the exchange-correlation with the generalized gradient approximation given by Perdew and Wang.¹⁹ The plane-wave cutoff energy is set to be 420 eV and the convergence of the energy is 10^{-3} eV. The Monkhorst-Pack scheme²⁰ is used to sample the Brillouin zone. The optimization of the lattice constants and the atom coordinates is made by minimization of the total energy. The separation distances for Ca adsorbates on carbon nanotubes and the defective graphene are set to be 11 Å, which is enough to make the systems isolated. All the structures are fully relaxed with a mesh of $1 \times 1 \times 5$ and the mesh of \mathbf{k} space is increased to $1 \times 1 \times 10$ to obtain accurate energies with atoms fixed after relaxations. We defined the binding energy of adsorbed atom as $E_b = (E_0 + nE_m - E_d)/n$, where E_d and E_0 are the energies per cell with and without atoms adsorbed and E_m and n are the energy and number of free adsorbate atoms, respectively.

III. RESULTS

We first investigate a single Ca atom on the (5,0) and (3,3) carbon nanotubes, as is shown in Fig. 1. These two tubes are

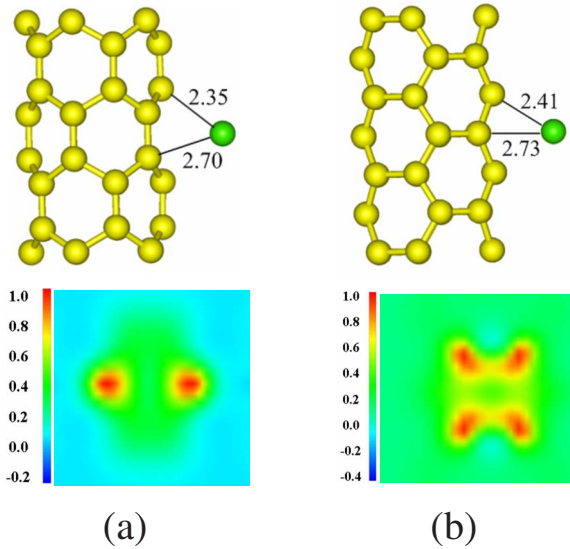


FIG. 1. (Color online) Structures and charge difference of Ca atom on carbon nanotubes: (a) Ca atom on the (5,0) tube; (b) Ca atom on the (3,3) tube.

ultranarrow carbon nanotubes with almost the same diameter.²¹ The unit cells are taken as two and four period lengths of the tubes for (5,0) and (3,3), respectively. It was believed that the stability of adsorption was enhanced by the curvature of carbon nanotube surface and the stability was increased as the diameter decreased. However, E_b for Ca atoms on the (5,0) tube is 2.64 eV, while E_b for Ca atoms on the (3,3) tube is only 1.27 eV. The binding-energy difference comes from the configuration of the surface. When a Ca atom is adsorbed on the (5,0) tube, there are two nearest-neighbor carbon atoms with distance of 2.35 Å and four next-nearest neighbors with distance of 2.70 Å. We obtain the charge difference by subtracting the charge density of the pure tube from that of the tube with Ca atom. As shown in Fig. 1(a), the charge transferred from the Ca atom is localized at the two carbon atoms, which are the nearest neighbors of the Ca atom. While for the case of the (3,3) tube, there are four nearest-neighbor carbon atoms with distance of 2.41 Å and two next-nearest neighbors with distance of 2.73 Å. As shown in Fig. 1(b), the charge transferred from Ca atom is localized at the four carbon atoms, which are the nearest neighbors of the Ca atom. We can deduce that the repulsion of negative charge on the (5,0) tube is smaller than that on the (3,3) tube, which enhances the stability of Ca adsorption.

We further show the stable Ca adsorbates with high coverage on carbon nanotubes. Figures 2(a) and 2(b) show the Ca adsorbates with the coverage of 1/2 on the (5,0) and (4,0) tubes. E_b are 1.62 and 1.94 eV, respectively, indicating that the stability of Ca adsorbates on the tubes with the same chirality is enhanced when the diameter of the tubes decreases. For Ca adsorbates with the coverage of 1/2 on the (6,0) and (7,0) tubes, E_b are 1.43 and 1.32 eV, respectively, which are higher than those of Ca on C_{60} .¹⁴ C_{60} with uniform Ca monolayer coated had been obtained experimentally.²² Thus, the Ca adsorbates on the (n ,0) ($n=4-7$) tubes are

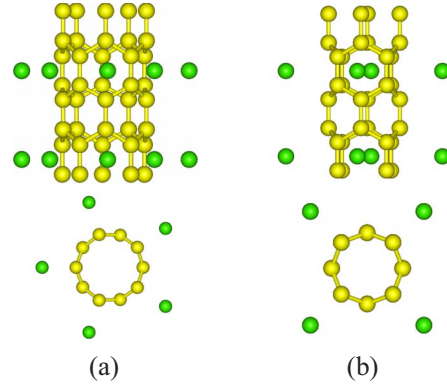


FIG. 2. (Color online) The stable Ca adsorbates on carbon nanotubes: (a) Ca adsorbates with the coverage of 1/2 on the (5,0) tube; (b) Ca adsorbates with the coverage of 1/2 on the (4,0) tube.

expected to be stable without clustering because the monolayers are formed when E_b is larger than or close to that of bulk metal. According to our calculations, E_b of bulk Ca is 1.70 eV while E_b is 1.20 eV for the Ca monolayer on C_{60} . Thus, the Ca monolayer on C_{60} is the metastable structure and Ca multilayers on C_{60} were also found.²² Generally, the instability of Ca adsorbates is caused by the electrostatic repulsion. When Ca atoms are adsorbed on the surfaces of carbon nanotubes, there is significant charge transfer from Ca atoms to carbon atoms. As the coverage becomes higher, the electrostatic repulsion is increased because of shortening of the Ca-Ca distance, which makes the system unstable. For narrow tubes, the surface curvature enlarges the Ca-Ca distance and thus enhances the stability of adsorbates with high coverage, which is similar to the potassium adsorbates on carbon nanotubes.²³ For the stable Ca adsorbates on carbon nanotubes, the Ca-Ca distance should be larger than that of bulk Ca, which is 3.82 Å. For the Ca adsorbates with the coverage of 1/2 on the (5,0) and (4,0) tubes, the nearest Ca-Ca distance is 4.26 Å and the next-nearest Ca-Ca distances are 4.93 and 5.40 Å. Higher E_b and larger Ca-Ca distance make Ca monolayers on the carbon nanotubes more stable than Ca multilayers. Previous works²⁷ showed that Li atoms can be adsorbed on the (5,0) tubes inside the zeolite experimentally. Thus, we assume that Ca atoms can be adsorbed on the (5,0) tubes in the similar way. However, the diameter of Ca atom is larger than that of Li atom and it might be difficult for Ca atoms to enter the interspace between the (5,0) tubes and the zeolite.

In the following, we investigate the interaction between hydrogen molecules and Ca dispersed tubes. We found that a single Ca atom on the (5,0) tube can adsorb up five H_2 , as shown in Fig. 3. When the first H_2 is adsorbed, the Ca- H_2 bond length is 2.49 Å and E_b is 0.25 eV, which is similar to the case of Ca dispersed C_{60} .¹⁴ E_b varies from 0.16 to 0.25 eV/ H_2 , dependent on the number of H_2 and the configurations. We found that there are two possible configurations for four adsorbed H_2 and the difference in E_b is quite small (about 0.04 eV/ H_2). We have repeated calculations of H_2 adsorption on Ca dispersed (4,0) tube and the results are similar. For simplicity, we focus on the H_2 adsorption on the

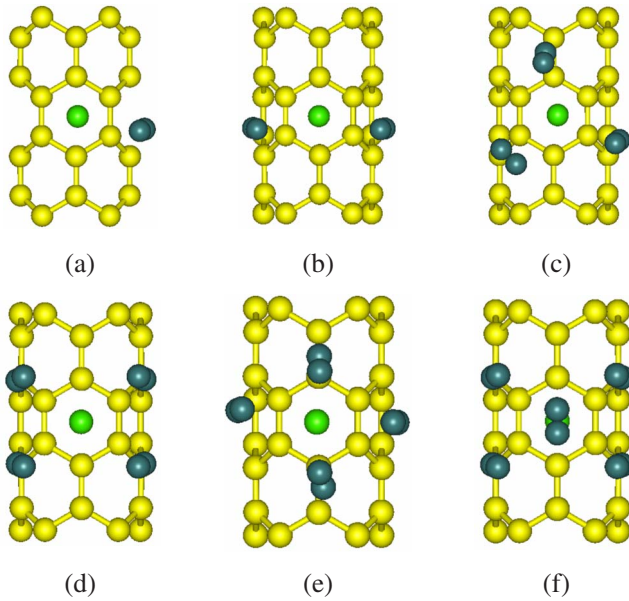


FIG. 3. (Color online) H_2 adsorption on the Ca dispersed (5,0) tube with different number (n): (a) $n=1$, $E_b=0.25$ eV; (b) $n=2$, $E_b=0.23$ eV; (c) $n=3$, $E_b=0.18$ eV; (d) $n=4$, $E_b=0.20$ eV; (e) $n=4$, $E_b=0.16$ eV; and (f) $n=5$, $E_b=0.17$ eV.

Ca dispersed (4,0) tube. The calculated binding energy is about 0.2 eV/ H_2 , which indicates that hydrogen storage can be achieved at ambient temperature and low pressure.^{7,14} We have also performed molecular-dynamics (MD) simulations on these Ca dispersed carbon nanostructures at 300 K for 1 ps. It was found that these nanostructures remained stable without significant deformation. When the Ca coverage is 1/2 on the (4,0) tube, the nearest Ca-Ca distance is along the axis of tube, as shown in Fig. 4(a). The Ca- H_2 bond length is 2.49 Å, which is much larger than that of Ti- H_2 .⁸ If there are five H_2 for every Ca atom, the distance between H_2 will be too small, making the system unstable. We have tested a few possible configurations with different numbers of H_2 and found that two Ca atoms can at most adsorb nine H_2 with E_b of 0.13 eV, as shown in Fig. 4(a). Similarly, when Ca coverage is 1/2 as shown in Fig. 4(b), eight Ca atoms can at most adsorb up 36 H_2 with E_b of 0.12 eV, corresponding to a hydrogen uptake of 9.3 wt %. Thus, the Ca dispersed carbon nanotubes are of potential for hydrogen storage. The Ca

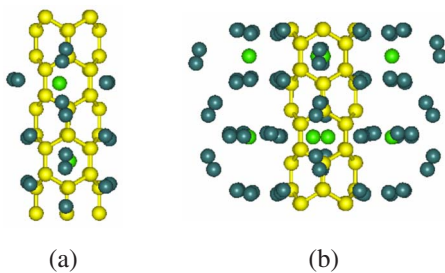


FIG. 4. (Color online) Hydrogen adsorption on Ca dispersed carbon nanotubes: (a) nine H_2 adsorption on the (4,0) tube coated with Ca chains; (b) 36 H_2 adsorption on the (4,0) tube with the Ca coverage of 1/2.

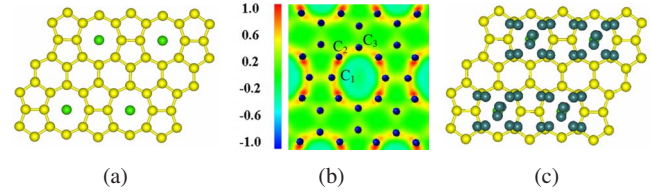


FIG. 5. (Color online) Stable Ca adsorbate on the defective graphene and the ability of hydrogen uptake. (a) The structure of CaC_5 ; (b) the charge difference of CaC_5 ; and (c) H_2 adsorption on CaC_5 .

monolayers on C_{60} achieve a hydrogen uptake of about 8.4 wt % (Ref. 14); however, in the crystal structure of $Ca_{32}C_{60}$, Ca atoms will form the linkage between clusters and lower the hydrogen storing capacity, which is similar to the case of $Li_{12}C_{60}$.¹² For carbon nanotubes, we assume that the intertubular distance can be enlarged by separating the tubes with the method of diffusion,²⁴ which might maintain the efficiency of hydrogen storage.

Our findings indicate that the stability of the Ca adsorbates depends on the configurations of surface and the distance between Ca atoms. We further discuss the stable Ca adsorbates on graphene with moderate defects and the application of hydrogen storage. It has been reported that various defect domains of graphene could be synthesized through the thermally activated restructuring of coalesced adatoms²⁵ and pyridinelike nitrogen-doped graphene can prevent the metal-atom aggregation, which has been shown to be optimistic for hydrogen storage.²⁶ As shown in Fig. 5(a), we consider the graphene with pentagonal and octagonal defects. We find that Ca atoms prefer to adsorb on the center of octagon and E_b is 2.18 eV. We have also considered the case that both sides of graphene are adsorbed with Ca atoms and found that E_b is reduced to 1.75 eV. The minimum of Ca-Ca distance is 4.97 Å, which is larger than that of Ca-Ca distance in the bulk (3.82 Å). Thus, this adsorbate is stable and the ratio of Ca:C is 1:5. Figure 5(b) shows the charge difference of the defective graphene with the Ca adsorbate. We have marked different kinds of carbon atom neighbors of a Ca atom with C_1 , C_2 , and C_3 and the distances of Ca- C_i are 2.68, 2.77, and 2.86 Å, respectively. We find that the charge transferred from the Ca atom is localized at the carbon atom marked with C_2 , which is the next-nearest neighbor of the Ca atom. If the charge is localized at the carbon atom marked with C_1 , the electrostatic repulsion will be strong and cause the instability of system. It is shown that the distribution of charge is the most important factor for the adsorption stability and the extra charge on adsorbent will stay apart from each other as far as possible. For the stable Ca adsorbate on the defective graphene, every Ca atom can adsorb up five H_2 with E_b of 0.08 eV, as is shown in Fig. 5(c). The Ca- H_2 distances are similar to the ones for Ca dispersed carbon nanotubes. The hydrogen uptake is 9.1 wt %; thus the Ca adsorbate on defective graphene can also be applied for hydrogen storage.

IV. SUMMARY

In summary, we show that Ca adsorbates on carbon nanotubes and defective graphene can be a potential hy-

drogen storage medium. We find that the adsorption stability depends on the distribution of charge, which depends on the surface configurations. We have predicted that the Ca adsorbates on carbon nanomaterials are highly stable without the tendency for clustering. The results show that every Ca atom can adsorb up four to five H₂, corresponding to a hydrogen uptake of over 9 wt %.

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