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Calcium decorated two dimensional carbon allotropes for hydrogen storage: A first-principles study

Rui Pan, Xiaoli Fan *, Zhifen Luo, Yurong An

State Key Laboratory of Solidification Processing, School of Material Science and Engineering, Northwestern Polytechnical University, 127 YouYi Western Road, Xi'an, Shaanxi 710072, China

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ABSTRACT

Graphene has attracted tremendous interest as a potential hydrogen storage medium due to its extraordinary properties granted by its two-dimensional nature. In this study, we investigated the hydrogen storage ability of five 2D carbon allotropes: C_{40}, C_{41}, C_{63}, C_{64} and C_{65} with calcium decoration by adopting the first-principles method based on density functional theory. The probable adsorption sites for a Ca atom and different Ca coverages were examined, and the hydrogen molecules were added one by one to investigate the maximum hydrogen gravimetric density. Our results show that Ca atom prefers to stay on the hollow site above the largest polygons instead of small polygons. Up to 6 hydrogen molecules can be adsorbed on one single Ca atom with the average adsorption energy in the reasonable range. The hydrogen gravimetric density for these carbon allotropes with Ca decoration are 3.53–4.48 wt.% at low Ca coverage and 7.5–8.57 wt.% at high Ca coverage.

1. Introduction

Currently, gradually increasing energy costs and environmental problems caused by fossil fuels are stimulating development of new, renewable energy sources. Among the many energy sources, hydrogen is a promising and environmentally friendly fuel and can be produced by many techniques [1]. The main problem with these technologies is that hydrogen is difficult to store and transport because it is easy to catch fire and explode. A safe and efficient way to store hydrogen is to adsorb hydrogen on the surface of materials with large surface areas at moderate condition. Recently, carbon-based nanomaterials, such as carbon nanotubes [2,3], fullerenes [4], and graphite nanofibers [5], have been reported as potential hydrogen storage media. Especially, experimental and theoretical studies have proved that metal-decoration is an efficient way to improve the hydrogen storage capacity as it can significantly increase the adsorption energy of hydrogen molecules on the decorated cabon-nanomaterials [6–13].

Alkali metals (AM) [6,7], alkali earth metals (AEM) [8–11], and transition metals (TM) elements [13], are often used to decorate the carbon-based nanomaterials to increase their hydrogen storage capacity. With a hydrogen storage uptake of 8.4 wt.% on calcium decorated fullerenes ($Ca_{32}C_{60}$), calcium has been concluded to be superior to all the other suggested metal elements to functionalize carbon nanomaterials for hydrogen storage [9]. This conclusion is supported by a theoretical study by Ataca et al. [10], where a gravimetric capacity of 8.4 wt.% has been predicted for calcium decorated graphene. Indeed, calcium has lower ionization potential and empty 3d orbitals, which makes charge transfer easily between Ca atom and the adsorbed C atoms, and the electric field induced by the charge redistribution functions as ideal attractors for H_2 molecules. Additional, it has been reported that the adsorption energies of isolated Ca atoms on carbon-based nanomaterials are comparable to its cohesive energy (1.84 eV/atom) of the bulk phase [8], which means that Ca atoms prefer to be dispersed on carbon-based nanomaterials instead of clustering together. All of these are important factors to make calcium a good decorator to achieve the high storage capacity.

Since the discovery of graphene, several two-dimensional (2D) carbon allotropes [14–21] and some other graphene-like compounds [22–24] have been reported. These 2D monolayer materials with special geometric structure and electronic properties hold promising potentials in the field of hydrogen storage. For example, in a study by Li et al. [15], Ca-decorated graphyne showed the high hydrogen storage capacity of 9.6 wt.%. Ye et al. [18] have reported lithium atoms can be dispersed homogeneously on T-graphene due to a nonuniform charge distribution and Li-decorated T-graphene can adsorb 7.7 wt.% H_2. In 2013, Lu and Li [25] theoretically predicted four new 2D carbon allotropes,

* Corresponding author.
E-mail address: xlfan@nwpu.edu.cn (X. Fan).

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which were named C_{41}, C_{63}, C_{64} and C_{65}, respectively. Later, Yadav et al. [26] studied the hydrogen storage on the Li-decorated C_{41}, C_{63}, C_{64} and C_{65}. By assuming the interaction between Li atom and the adsorbed C atoms will be weak on the largest polygon, Li atom has been positioned on the small polygon. They find that the Li-decorated C_{41} produce the highest hydrogen gravimetric density of 7.12 wt.%. Due to the non-delocalized sp2-carbon structure and nonuniform charge distribution on these new 2D carbon allotropes, it is very necessary to study the adsorption of other metal atoms and hydrogen storage on them.

In the present study, by performing the first-principles calculations, we studied the hydrogen storage of five Ca decorated 2D carbon allotropes: T-graphene (denoted as C_{40}), C_{41}, C_{63}, C_{64} and C_{65}. We firstly examined the possible adsorption sites of Ca atom on C_{40}, C_{41}, C_{63}, C_{64} and C_{65}. Then we calculated the adsorption of hydrogen on these 2D carbon allotropes with calcium decoration. To investigate the maximum hydrogen storage density, we studied the cases of hydrogen adsorption on both sides of the monolayers as well as the high coverage decoration. The van der Waals (vdW) interaction between the adsorbed hydrogen molecules and the carbon substrates were calculated by the vdW-DF2 functional [27]. We have found that Ca atom prefer to stay above the largest polygon instead of the small polygon, unlike Li atom reported in the previous study [26]. Our calculation results show that each Ca atom can bind up to six hydrogen molecules in the reasonable energy range, and the Ca-decorated C_{64} produces the highest hydrogen gravimetric density of 8.57 wt.%.

2. Computational methods

All the calculations in the present study were carried out by using the Vienna *ab-initio* simulation package (VASP) [28] with the Perdew–Burke–Ernzerh of generalized gradient approximation (GGA) exchange-correctional function [29]. The electron-ion interactions were calculated by the projector augmented wave (PAW) method [30]. The kinetic energy cutoff value was set to 500 eV and the first Brillouin zone was sampled by the Monkhorst-Pack [31] method. The simulations were carried by a $3 \times 3 \times 1$ k-grid for the (3×3) supercell of C_{40}, and (2×2) supercells of C_{41}, C_{63}, C_{64} and C_{65}, as well as $(\sqrt{3} \times \sqrt{3})$ supercells of C_{63}, C_{64} and C_{65}. A precise $5 \times 5 \times 1$ k-grid was used for the (2×2) supercell of C_{40}. A vacuum layer of 20 Å along the vertical direction to the monolayers was employed to avoid interaction between periodic images. The minimum energy path (MEP) was calculated by climbing image nudged elastic band method (CINEB) developed by the Jónsson group [32]. During the total energy and MEP calculations, the total energy tolerance was set as 10^{-5} eV, and all the atoms were allowed to fully relax until the force on each atom was less than 0.02 eV/Å. Electronic orbitals of 1s, 3p4s and 2s2p were considered as valence states for H, Ca and C atoms, respectively.

It is well recognized that the PBE-GGA function generally provide an accurate description for ionic, metallic and covalent materials, but it will be quite inaccurate for the van der Waals systems. Several methods have been proposed to represent the weak interactions, such as DFT-D [33], DFT-TS [34] and vdW-DF [35]. Among these methods, the vdW-DF method provides a generalized truly nonlocal functional independent of system geometry. While, the vdW-DF2 functional was reported to be more accurate than vdW-DF in estimating equilibrium separations, hydrogen bond strengths and van der Waals attraction at longer intermediate separations. More importantly, the vdW-DF2 functional predicts the most reasonable results for molecules adsorption on metal surfaces [36], especially, hydrogen molecules on copper surfaces [37]. Thus, we use vdW-DF2 method to correct the total energies of hydrogen molecules adsorption on calcium decorated carbon allotropes. The exchange-correlation energy in vdW-DF2 method is defined as

$$E_{xc}^{vdW} = E_x^{GGA} + E_c^{LDA} + E_c^{nl} \quad (1)$$

where E_x^{GGA} is the GGA exchange energy, E_c^{LDA} is the LDA short-range correlation energy, and E_c^{nl} describes the nonlocal (long-range) exchange contribution.

3. Results and discussions

3.1. 2D carbon allotropes

Fig. 1 shows the five 2D carbon allotropes, C_{40}, C_{41}, C_{63}, C_{64} and C_{65}. As shown in Fig. 1, C_{40} is the network of C_4 square, and C_{41} is the network of C_4 square and C_1 (sp2-hybridized carbon atom) units. For the hexagonal carbon allotropes of C_{63}, C_{64} and C_{65}, the C_6 hexagons are connected by C_3 triangles, C_4 squares and C_5 pentagons, respectively. According to the previous studies, all of these structures are not only dynamically stable but also more favorable energetically than graphyne [19,25]. Our calculation results for the five carbon monolayers are illustrated in Table 1, which agree well with the previous studies [19,25].

3.2. Adsorption of calcium atom on carbon allotropes

As we have mentioned in the introduction part, Ca has been found to be superior to other metal atoms in decorating carbon-based nanomaterials for hydrogen storage. To study the hydrogen storage of Ca decorated C_{40}, C_{41}, C_{63}, C_{64} and C_{65}, we firstly studied the adsorption of one single Ca atom on the five carbon allotropes. For C_{40}, the (3×3) surpercell with one Ca atom adsorption corresponds to 2.78% Ca coverage. And the (2×2) supercell with one Ca adsorption represents the coverage of 2.08% for C_{41}, C_{63} and C_{64}, and 2.5% for C_{65}.

Three high symmetry sites: top site (T), bridge site (B) and hollow site (H) were considered for Ca adsorption. As we know, these allotropes are the networks of differently sized polygons as shown Fig. 1. In this context, the hollow sites above the small, medium and large polygons were all examined. They are named as H1, H2 and H3, respectively. For example, H1, H2 and H3 of C_{65} represent the hollow site above the pentagon, hexagon and nonagon. The adsorption energies are calculated as

$$E_{b\_Ca} = \left[\left(E_{C_{al}} + nE_{Ca}\right) - E_{nCa+C_{al}}\right]/n \quad (2)$$

where $E_{C_{al}}$ and E_{Ca} represent the total energy of the carbon allotrope sheet and the free Ca atom, respectively. $E_{nCa+C_{al}}$ is the energy of Ca-decorated carbon allotrope, and n is the number of Ca atoms adsorbed on the allotropes.

The calculation results for Ca adsorption on the five carbon allotropes are summarized in Table 2. According to our calculations, the Ca atom transforms atomically from the top site and bridge site to the nearest hollow site during the total energy calculations. Thus, Table 2 only lists the adsorption energies of Ca on the hollow sites. However, there is one exceptional top site that is the center of the three adjacent pentagons on C_{65}. It is denoted as T^* as shown in Fig. 1(e). After structural optimization, Ca atom transforms atomically from the H1 site above the pentagon to the T^*, and the adsorption energy of Ca on T^* is larger than the adsorption energy on H2 above the hexagon. As listed in Table 2, all of the adsorptions on the hollow sites and the T^* site give positive binding energies, it means that these adsorptions are energetically favorable. The average distances between the adsorbed Ca atom and the nearest carbon atoms are 2.53–2.55 Å for C_{40}, C_{41}, C_{63}, and C_{65}. As we can see from Fig. 1, the largest polygon in C_{64} is the circle of 12 C atoms. In this case, the Ca atom is embedded in