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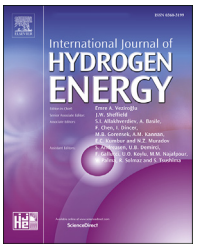

A novel hydrogen storage medium of Ca-coated B_{40}: First principles study

Yafei Zhang, Xinlu Cheng *

Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, 610065, PR China

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ABSTRACT

Using first principles study, we have investigated the hydrogen storage capacity of Ca-coated B_{40}. Our result shows that Ca prefers to adsorb on the top hollow center of heptagonal ring of B_{40} due to the large binding energy of −2.820 eV. Bader charges calculation indicates that charges transfer from Ca to B_{40} result in an induced electric field so that H_2 molecules are polarized and adsorbed onto the surface of B_{40} without dissociation. The Ca_6B_{40} complex can adsorb up to 30 H_2 molecules with average adsorption energy of −0.177 eV/H_2 and the hydrogen storage gravimetric density reaches up to 8.11 wt.%, higher than the goal from DOE by the year 2020. These findings will suggest a new and potential structure for hydrogen storage in the future.

Introduction

Boron, as the fifth element in the periodic table, has received extensive attention and been extremely explored for many boron-based porous nanomaterials, such as boron nanowires [1], boron sheets [2], boron fullerenes [3–5], boron nanotubes [6] and so on. Meanwhile, these boron-based porous nanostructures are considered as promising hydrogen storage materials due to their chemical stability with large specific surface area as well as light weight [7–9]. Hydrogen has been recognized an ideal clean energy with much abundant and will replace the traditional fossil fuel energy in the near future [10]. Also, it is no pollution to the environment because the product of combustion is water. The range of ideal hydrogen adsorption energy should be between 0.1 and 0.2 eV/H_2 to realize hydrogen adsorption and desorption at room temperature [11,12]. Moreover, it is necessary for us to discover and design the high capacity hydrogen storage medium to meet the goal of 5.5 wt.% hydrogen storage gravimetric density for vehicle applications from U.S. Department of Energy (DOE) by the year 2020 [13].

As for hydrogen adsorption, it is found that the pure nanostructures cannot be used for hydrogen storage because of the weak interaction force of van der Waals (vdW) between the H_2 molecules and host nanostructures [14,15]. In order to improve the adsorption ability for H_2 molecules, metal doping is proven to be an effective and practical method. Such as alkali and alkaline-earth metals (AM) decorated B_{38} and C_{24} [16,17], transition metals (TM) decorated B_{40} and B_{38} [18,19], graphene nanoribbons [20,21], carbon nanotubes [22], and light metal Li decorated phosphorene [23] and so on. In this situation, the H_2 molecule is adsorbed around the metal atom by physical or chemical adsorption. Of course, the big challenge for us is how to prevent adsorbed metal atoms from aggregation [24,25]. In the past few years, boron-based

* *Corresponding author.*
E-mail address: chengxl@scu.edu.cn (X. Cheng).

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nanostructures are widely studied for hydrogen storage by using first principle based density functional theory calculation.

Li et al. [26] studied the high-capacity hydrogen storage of magnesium-decorated B_{80} fullerene and found that 96 H_2 molecules can be adsorbed around $Mg_{12}B_{80}$ complex with adsorption energy of 0.20 eV/H_2 and the H_2 storage capacity of 14.2 wt.%. Lu et al. [16] demonstrated the hydrogen storage capacity of alkali and alkaline-earth metal (Li, Na, K, Mg and Ca) decorated B_{38} fullerene and showed Ca-decorated B_{38} was feasible and remarkable for high capacity storage. They found that each Ca could hold up to five H_2 molecules and 20 H_2 molecules were adsorbed near the Ca_4B_{38} complex with the desirable adsorption energy of 0.24 eV/H_2 and the hydrogen storage capacity reached up to 6.47 wt.%. Chen et al. [27] investigated the hydrogen adsorption properties of Ca-decorated borophene and found that Ca atoms had strong bonding strength with borophene without aggregation and two configurations of Ca-decorated borophene (S2 and S3) were promising storage mediums with high hydrogen density of 9.5 wt.% and 7.2 wt.%, respectively. Moreover, boron nanotubes are also proven as outstanding candidates for hydrogen storage applications [28]. An et al. [29] reported the hydrogen storage behavior in Li-coated radial deformation zigzag boron nanotubes and indicated the hydrogen storage density reached up to 7.94 wt.% with the hydrogen adsorption energy from 0.12 to 0.20 eV/H_2.

Recently, Zhai et al. [4] reported the observation for all-boron fullerene-like cage cluster at B_{40}^- by using photoelectron spectroscopy. The neutral counterpart B_{40} fullerene demonstrates high symmetry (D_{2d}) and has an excellent thermal stability at temperature of 1000 K under dynamics simulation. Meanwhile, the B_{40} fullerene has received widely investigations for hydrogen storage application so far. Tang et al. [18] studied Sc atoms decorated porous B_{40} fullerene could serve as high capacity hydrogen storage medium. Five H_2 molecules were adsorbed around each Sc atom and hydrogen storage density was 6.18 wt.% with the adsorption energy from 0.33 to 0.58 eV/H_2. Liu et al. [30] calculated alkali metal (AM = Li, Na, K) decocted B_{40} fullerene and the results showed that the hydrogen storage density of Li_6B_{40}, Na_6B_{40} and K_6B_{40} complexes were 7.8 wt.%, 8.4 wt.% and 8.8 wt.%, respectively, and exceed the goal from the DOE of 5.5 wt.% by the year 2020. In addition, small boron cluster is also favorable for hydrogen storage in the recent study [31].

In this article, the hydrogen storage capacity of Ca-coated B_{40} has been studied by first principles calculation. We firstly seek the stable adsorption site for Ca and the result shows the favorable site is the top center of the heptagon of B_{40}. Next, we calculate H_2 adsorption properties and maximal hydrogen storage density. Finally, H_2 adsorption mechanism and desorption performance are investigated and the conclusion indicates Ca-coated B_{40} can as a candidate for hydrogen storage medium at near-ambient conditions.

Computational details

The first principles calculations of our work were performed by using Vienna Ab-initio Simulation Package (VASP) [32,33] based on the density functional theory (DFT). The Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA) function [34] was adopted to describe the exchange and correlation energy with the projector augmented wave (PAW) method [35,36]. Moreover, the K points grid of Brillouin zone (BZ) used 4 × 4 × 4 Monkhorst-Pack mesh and the kinetic energy cutoff of plane wave was 350 eV. The valence electrons configurations were set to H ($1s^1$), B ($2s^2 2p^1$), and Ca_sv ($3s^2 3p^6 4s^2$), respectively. Also, the DFT-D2 method was used to consider the van der Waals (vdW) dispersion correction [37,38] and the convergence thresholds value were set to 10^{-5} eV for energy and −0.05 eV/Å for force, respectively.

In order to confirm the accuracy for our study, we calculate the binding energy (△E) and H—H bond length for an isolated H_2 molecule, the results are 4.518 eV for bing energy and 0.751 Å for H—H bond length. They are in good agreement with the experimental value of 4.53 eV and 0.74 Å, respectively [39].

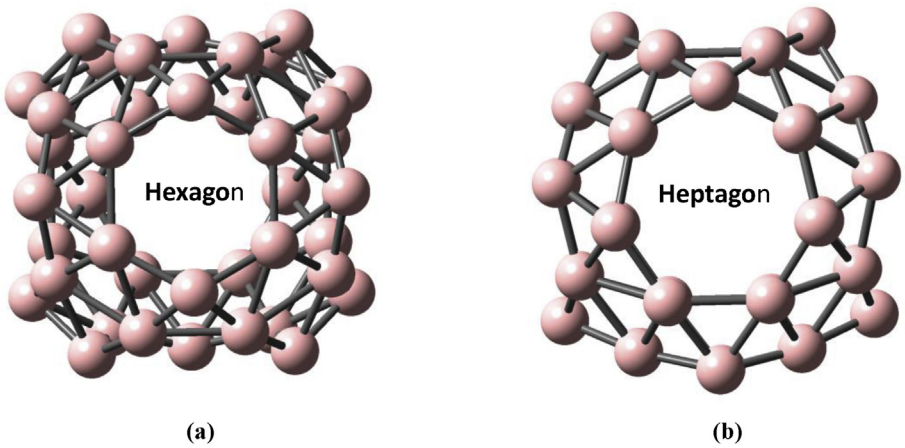

Fig. 1 – The optimized structure of B_{40}, (a) one hexagon is surrounded by four heptagons and (b) one heptagon is surrounded by two hexagons and two heptagons.

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