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Hydrogen storage property of alkali and alkaline-earth metal atoms decorated C_{24} fullerene: A DFT study

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ABSTRACT

The hydrogen storage behavior of alkali and alkaline-earth metal (AM = Li, Na, K, Mg, Ca) atoms decorated C_{24} fullerene was investigated by using density functional theory (DFT) study. Our results indicate that the AM atoms prefer to adsorb atop the center of tetragon of C_{24} fullerene with the largest binding energy than other possible adsorption sites. Moreover, the hydrogen storage gravimetric density of $24H_2/6Li/C_{24}$, $24H_2/6Na/C_{24}$ and $36H_2/6Ca/C_{24}$ configurations reaches up to 12.7 wt%, 10.1 wt% and 12 wt%, higher than the year 2020 target from the US department of energy (DOE). Also, the average adsorption energies of H_2 molecules of the $24H_2/6Li/C_{24}$, $24H_2/6Na/C_{24}$ and $36H_2/6Ca/C_{24}$ configurations are -0.198 eV/H_2, -0.164 eV/H_2 and -0.138 eV/H_2, locate the desirable range under the physical adsorption at near ambient conditions. These findings will have important implications on designing new hydrogen storage materials in the future.

1. Introduction

As we all know, energy plays an important role in our daily life, but with the large use of traditional fossil fuels, greenhouse effect, acid rain and PM2.5 particles seriously threaten human survival and development. Hydrogen had been recognized an ideal clean energy with its much abundant storage and high heat thermal capacity on the earth [1–3]. Also, it is necessary for us to design and fabricate new efficient and safe hydrogen storage materials to decrease environment pollution and fossil fuels consumption. Moreover, to improve the hydrogen storage capacity and realize reversible adsorption and desorption under ambient conditions become great challenges for us [4]. The excellent adsorption energy of hydrogen molecules should lie between -0.1 eV and -0.6 eV is desirable for the reversible hydrogen adsorption and desorption at near ambient conditions [5]. The U.S. Department of Energy (DOE) set a target for the ideal hydrogen storage materials should reach to 5.5 wt% gravimetric density by the year 2020 [6].

Helden et al. [7] observed C_{24} and C-24 cluster by using the experimental methods for the first time in 1993. Akhtar et al. [8] produced C + 24 cluster in a graphite hollow cathode based duoplasmatron and the mass analysis with low energy heavy ion detected method in 2003. What is more, Oku et al. [9] observed an atomic structure model of $C_{24}@C_{84}$ cluster in the experiment and small C_{24} clusters played a catalytic role. An et al. [10] studied the chemical stability of six low-energy isomers of C_{24} cluster from global-minimum search and found one classical fullerene composed of only five- and six-membered rings, three nonclassical fullerene contains one four-membered ring at least, one plate and one monocyclic ring based on density functional theory calculation. Wu et al. [11] reported two kinds of common isomers of C_{24} cluster, one is an O_h symmetry formed by eight hexagonal rings and six tetragonal rings, and the other is a D_6 symmetry formed by twelve pentagonal rings and two hexagonal rings. Although the D_6 symmetry had been proved more stable than the O_h symmetry in terms of binding energy per atom (E_b) based on density functional theory calculation [12], but the HOMO–LUMO gap (E_g) of O_h symmetry is 2.35 eV, higher than D_6 symmetry of 1.82 eV [11]. Therefore, the O_h symmetry of C_{24} cluster also has a strong stability.

Because of the van der Waals (vdW) force has a weak interaction on the surface of pure nanostructures with hydrogen molecules and result in the surfaces cannot adsorb hydrogen molecules efficiently [13]. Researchers found that these pure nanostructures modified by the metal atoms can improve the adsorption ability of hydrogen molecules [14–16]. From the previous study, carbon-based nanomaterials are considered as excellent hydrogen storage candidates and widely explored for their application in hydrogen storage field [17–19]. A remarkable hydrogen storage system should not only include the desirable adsorption energy for H_2 molecules but also obtain high hydrogen storage density. If the adsorption energy for H_2 molecules is too low and

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do not locate the suitable range, it will not guarantee the adsorption is valid for the adsorbed H_2 molecules [20]. Moreover, it is difficult for hydrogen molecules to release under the situation of chemical adsorption from metal hydrides [21], because the adsorbed H_2 molecules are dissociated to form carbon hydrides and stored in atomic form. In addition, it is necessary to receive high hydrogen storage density, in our study, the AM decorated C_{24} structures can realize higher hydrogen storage density than other carbon-based nanomaterials, such as Ca decorated C_{60} fullerene with hydrogen storage density of 8.4 wt% [22], Na decorated C_{60} fullerene with hydrogen storage density of 9.5 wt% [23], light metal Li decorated on both sides of double carbon vacancy graphene (DVG) with 7.26 wt% [24] and so on.

In this article, we have investigated the H_2 adsorption property of AM atoms decorated C_{24} fullerene by using density functional theory study. Through our calculation, we conclude that the top center of tetragon of C_{24} fullerene is the favorable site for AM atoms to adsorb and metal clusters is avoided due to the large binding energy with the host material. Meanwhile, the adoption performance of H_2 molecules is calculated for the case of single and uniform decoration by AM atoms of C_{24} fullerene.

2. Computational methods

In our study, the geometry optimization and property calculation was obtained from DMol^3 package with double numerical basis sets and polarization function (DNP) adopted based on density functional theory (DFT) [25,26]. Meanwhile, the generalized gradient approximation (GGA) with Perdew, Burke and Ernzerhof (PBE) function was employed to describe the exchange and correlation function [27]. In the process of geometric optimization, a global orbital cut off of medium precision was chosen and van der Waals (vdW) interaction was considered by using Grimme method for DFT-D correction [28,29]. Because it contains the long range dispersion energy correction and can obtain better effect in many hydrogen storage systems [30–33]. Moreover, the threshold value for the convergence tolerance of energy, the maximum force and the max displacement were set to 2.0×10^{-5} Ha, 0.004 Ha/Å and 0.005 Å in geometry optimization, respectively. In addition, the systems were calculated under unrestricted spin and without any symmetry constraints and smearing value of 0.005 Ha (1 Ha = 27.2114 eV) was chosen to speed up the geometry optimization.

The binding energy of decorated AM atom is calculated by the following equation

$$E_b = [E_{mAM+C_{24}} - E_{C_{24}} - mE_{AM}]/m \tag{1}$$

where $E_{mAM+C24}$, E_{C24} and E_{AM} are the total energy with m AM atoms adsorbed on C_{24} fullerene, the total energy of C_{24} fullerene, and the total energy of an isolated AM atom, respectively. The average adsorption energy (E_{ads}) and consecutive adsorption energy (E_c) of per H_2 molecule are used these two equations

$$E_{ads} = [E_{nH_2+mAM+C_{24}} - E_{mAM+C_{24}} - nE_{H_2}]/n \tag{2}$$

$$E_c = [E_{nH_2+mAM+C_{24}} - E_{(n-1)H_2+mAM+C_{24}} - E_{H_2}] \tag{3}$$

where $E_{nH2+mAM+C24}$, $E_{(n-1)H2+mAM+C24}$, $E_{mAM+C24}$ and E_{H2} are the total energy of the system with n H_2 and $(n-1)$ H_2 molecules adsorbed, the total energy of AM decorated C_{24} fullerene and the total energy of an isolated H_2 molecule, respectively. Moreover, the consecutive adsorption energy (E_c) indicates the adsorption energy of the nth hydrogen molecule, if the consecutive adsorption energy for the nth hydrogen molecule is too small that will result in the adsorption ability for the nth hydrogen molecule is invalid [34–36].

In order to confirm the accuracy of our methods, we calculate the bond length and binding energy of an isolated H_2 molecule with PBE function and find the value of bond length is 0.752 Å with binding energy of 4.553 eV, which is in good agreement with the experimental study of 0.74 Å and 4.53 eV [37,38]. Therefore, our calculation is reasonable and credible.

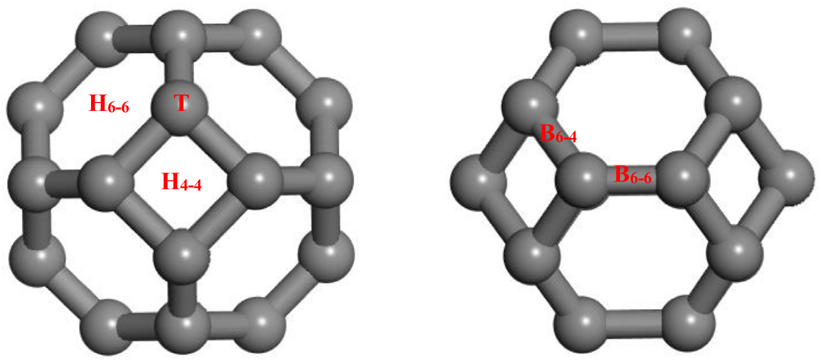
3. Results and discussion

3.1. The vibration frequency and optimized structure of C_{24} fullerene

The C_{24} fullerene has a high symmetry and consists of six tetragons and eight hexagons. The calculated vibration frequency of C_{24} fullerene is in the range from 369.52 to 1577.07 cm^{-1} with position number and no any imaginary frequency appears. So, the structure of C_{24} fullerene is proven more stable. Also, after geometry optimization, there are two kinds of bonds length among 36C—C bonds in C_{24} fullerene as displayed in Fig. 1. One kind of bond length is 1.49 Å between tetragon and hexagon and the other kind of bond length is 1.38 Å between two hexagons, which is in good agreement with the former study [11].

3.2. AM decorated C_{24} fullerene

In order to find out where is the most stable site for alkali and alkaline-earth metal (AM) atoms to adsorb, we explore such possible adsorption sites, atop the center of hexagon ($H_{6\text{-}6}$), atop the center of tetragon ($H_{4\text{-}4}$), atop the C—C bridge between two



(a) (b)

Fig. 1. The optimized structure of C_{24} fullerene with O_h symmetry, (a) top view and (b) side view.