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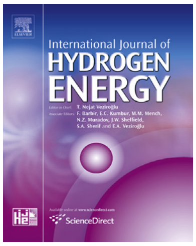

Li-decorated graphyne as high-capacity hydrogen storage media: First-principles plane wave calculations

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ABSTRACT

Taking into account the van der Waals correction, the characteristics of the Li-decorated graphyne as the hydrogen storage medium have been explored using first-principles plane wave calculations. We find that Li atom can be adsorbed not only over the center of large hexagon (H_L site) but also over the center of small hexagon (H_S site). For double-side Li decorations, there are $14H_2$ molecules can be adsorbed on Li-decorated graphyne primitive cell with the adsorption energy of 0.19 eV/H_2. As a result, the hydrogen storage capacity of 13.0 wt% can be obtained. This suggests that the Li-decorated graphyne system can serve as a high-capacity hydrogen storage medium.

Introduction

Hydrogen would be ideal as a synthetic fuel because it is lightweight, highly abundant and its oxidation product (water) is environmentally benign. So, hydrogen energy is considered to be an ideal clean energy source that could one day replace fossil fuels to resist environment pollution [1]. However, the storage of hydrogen remains a problem. One of the most difficult challenges is to find a proper material with high density hydrogen storage. Recently, the adsorption of hydrogen on carbon based nanomaterials, such as graphene [2,3], carbon nanotube [4,5] and so on, has been studied. These carbon species are suggested to be the promising hydrogen storage medium due to their lightweight and large surface area. Unfortunately, the adsorption of hydrogen molecule (H_2) on these pristine C-based nanostructures is very weak. In order to enhance the strength of binding between hydrogen molecules and substrate, the metal doping or decorating has been proposed [6–10]. For instance, the binding energies increase to 160–180 meV/H_2 from 80 to 90 meV/H_2 for the Li-decorated carbon nanotube and graphene [11]. On the other hand, from practical application point of view, it is favored for the hydrogen storage materials to possess the smaller volume and lighter gravimetry. To meet the minimum volumetric and gravimetric requirements, nowadays considerable efforts have been devoted to explore the lighter storage materials.

Graphyne, a new allotrope of carbon which connected with sp^2 and sp^1 hybridized carbon atoms, was first predicted by Baughman et al., in 1987 [12]. Subsequently, various types

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(graphyne [13] and graphdiyne [14]) and dimensions (3D [15,16], 2D [17], 1D [18–21], and 0D [22]) of graphyne-like networks have been proposed. Since large-area graphdiyne films [23], nanowires [24], and nanotubes [25] have been successfully grown experimentally, graphyne has attracted increasing attention and research interest. For example, first-principle calculations indicated that graphynes also possess Dirac cones, and 6,6,12-graphyne has direction-dependent Dirac cone, suggesting that the electronic property of this material is more amazing than that of graphene [26]. In addition, the simulations by classical molecular dynamics (MD) predicted that the graphene sheets are very stable in the temperature range from 300 to 1000 K, but they quickly turn into graphene if the temperature is above 2000 K [27]. Especially, these flat carbon networks ($sp^2 + sp^1$) with uniformly distributed pores are considered as possible promising materials for energy storage applications and otherwise [28–30].

Recently, Li et al. [31] chose Ca-decorated graphyne for probing this material as a possible template for hydrogen storage. Their results show that the maximal binding number of H_2 to each Ca atom remains six, the hydrogen capacity is estimated to be 9.6 wt% for double-side Ca decorations, and the H_2 binding energy is 0.2 eV. More recently, Lee et al. [32] reported another type of graphyne network decorated with Ca atoms as promising hydrogen storage media. They found that five H_2 molecules can be adsorbed on a Ca atom with a binding energy of ~0.2 eV, and the hydrogen storage capacity is ~7 wt%. In fact, in order to obtain a sufficiently high gravimetric density, not only the substrates need to be lightweight materials, but also the decorating metals need to be lightweight. Recent studies address that the Li atom is the better candidate as the decorating metal atom for improving the hydrogen storage [33–36]. To our best knowledge, so far there have been two reports about the hydrogen adsorption properties of Li-dispersed graphyne. One predicted a gravimetric density of 6.5 wt% for hydrogen adsorption [37], and the other repots the gravimetric density of 15.15 wt% [38]. However, the results are questionable for these two studies. On one hand, the occupied sites of the Li atoms in the former work are within the graphyne plane, which is not reasonable, and significantly in conflict with those reported by Zhang et al. [39] Therefore, the results reported in the former paper are debatable. On the other hand, the calculations in the latter work are at the level of local density approximation (LDA), which always overestimates the binding energy. In order to properly estimate the gravimetric density for the hydrogen molecule adsorption, the van der Waals (vdW) correction should be considered. Therefore, further theoretical work is necessary.

As we know, an ideal hydrogen storage system would be the one with a binding energy between those of physisorption and chemisorption energies. This ensures that a significant amount of hydrogen molecules can be efficiently adsorbed and to release them without difficulty under operating conditions. Physisorption essentially depends on electrostatic or non-local van der Waals interactions. Hence, it is very important to consider the vdW corrections when simulating the hydrogen adsorption systems. In the past, the vdW corrections were always omitted due to the DFT calculations' inability to describe the vdW interactions. Fortunately, the current state-of-the-art of the calculation in hydrogen storage can well describe the vdW interactions since Grimme S. [40] have considered the vdW forces within the DFT calculations and implemented in the VASP code.

In this paper, considering the vdW correction, we have investigated the hydrogen storage behavior on the Li-decorated graphyne by first-principles plane wave calculations to foresee the maximal hydrogen storage capacity. We find that the Li atom, either at H_L site or at H_S site, can both adsorb H_2 molecules. For double-side Li decorations, our calculations predict a maximum hydrogen storage capacity of 13.0 wt% with the average adsorption energy of 0.19 eV. This suggests that the Li-decorated graphyne is a promising candidate as high-capacity hydrogen storage materials.

Computational details

All calculations are performed using the Vienna *ab initio* simulation package (VASP) [41,42] within the projector augmented wave (PAW) approach [43,44]. The exchange-correlation part is described with the Perdew-Burke-Ernzerhof (PBE) [45] functional. The Monkhorst-Pack meshes [46] of 6 × 6 × 2 are used in sampling the Brillouin zone for the (1 × 1) graphyne primitive cell. A vacuum region of 20 Å in the z-axis direction is employed, which is sufficiently large to neglect the interaction between images caused from the periodic boundary condition. The energy cutoff for the plane waves is chosen to be 600 eV. The entire systems are fully relaxed by conjugate gradient method until the force on each atom is less than 0.01 eV/Å. In our treatment about the vdW correction, the DFT-D2 method of Grimme [40] has been employed. In which, the cutoff radius for pair interactions is selected to be 30.0 Å, the global scaling factor that has been optimized at the level of PBE functional is 0.75, and the damping parameter is set to be 20.0. More importantly, the validity of this scheme in the study of hydrogen storage in Ca-graphyne, Metal-dispersed porous graphene, Boron-substituted graphyne and so on has been demonstrated in the previous works [31,32,47,48].

In this paper, the average binding energy (E_b) of n Li atoms binding to the graphyne, the average adsorption energy (E_{ad}) of m H_2 molecules adsorbing on the Li-dispersed graphyne, the sequential adsorption energy (ΔE) of H_2 molecules (the adsorption energy of the mth H_2 molecule) and the sequential binding energy ($\Delta E'$) of Li atom (the binding energy of the nth Li atom) are respectively defined as.

$$E_b = \left(nE_{\mathrm{Li}} + E_{\mathrm{graphyne}} - E_{n\mathrm{Li+graphyne}}\right)/n, \tag{1}$$

$$E_{\mathrm{ad}} = \left(mE_{\mathrm{H_2}} + E_{n\mathrm{Li+graphyne}} - E_{m\mathrm{H_2}+n\mathrm{Li+graphyne}}\right)/m, \tag{2}$$

$$\Delta E = E_{\mathrm{H_2}} + E_{(m-1)\mathrm{H_2}+n\mathrm{Li+graphyne}} - E_{m\mathrm{H_2}+n\mathrm{Li+graphyne}}, \tag{3}$$

$$\Delta E' = E_{\mathrm{Li}} + E_{(n-1)\mathrm{Li+graphyne}} - E_{n\mathrm{Li+graphyne}}, \tag{4}$$

where the "n" and "m" are the number of Li atoms and H_2 molecules, respectively. $E_{n\mathrm{Li+graphyne}}$ and $E_{m\mathrm{H_2}+n\mathrm{Li+graphyne}}$ are the total energies without and with H_2 molecules adsorbed on the Li-decorated graphyne, respectively. $E_{\mathrm{H_2}}$ and E_{Li} are the total