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External electric field: An effective way to prevent aggregation of Mg atoms on γ-graphyne for high hydrogen storage capacity

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ABSTRACT

In this article, we investigate the hydrogen storage capacity of Mg-decorated γ-graphyne (Mg-G) based on DFT calculations. Our results indicate that an external electric field can effectively prevent Mg atoms aggregating on γ-graphyne sheet. The Mg-G, after electric field (F = 0.05 V/nm) treatment, can store up to ten H_2 molecules and the hydrogen storage capacity is 10.64 wt%, with the average adsorption energy of 0.28 eV/H_2. Our calculations demonstrate that Mg-G is a potential material for hydrogen storage with high capacity and might motivate active experimental efforts in designing hydrogen storage media.

1. Introduction

Hydrogen is considered to be an ideal clean energy source to replace fossil fuels for its high combustion value, rich resources and non-pollution property. However, finding materials to store hydrogen safely and economically is still a challenging problem [1,2]. A desired hydrogen storage system should meet two main criteria: high gravimetric density (>5.5 wt%), and the adsorption energy of the hydrogen molecule should be between −0.20 and −0.70 eV at room temperature [3]. In recent years, growing attention has been focused on the metal-decorated carbon nanotubes, C_{60} fullerenes, graphenes [4–8]. The decorating atoms can be transition metals, alkaline metals, or alkaline earth metals [9–15]. However, transition metal atoms prefer to form clusters when they are on the substrate [16–19]. Alkali and alkaline-earth metals are proposed as uniform coating due to their small cohesive energies and light weight. Unfortunately, among the alkali and alkaline-earth metals, Mg is not be commonly used. The binding energy of the Mg on the carbon substrates is so weak that an obvious aggregation occurs [20,21]. Reunchan. et al. [20] have studied alkaline metals and alkaline-earth metals doped porous graphene, all metal atoms except Mg were found to bind to porous graphene with 0.2 eV, which is much smaller than the Mg metal cohesive energy (E_{coh}) of 1.51 eV [22]. Dong et al. [21] calculated binding energy of Mg atoms on saddle-shaped nanographene is only about 0.4 eV.

Graphyne, a novel allotropic form of carbon, was predicted to have a high possibility of synthesis by Baughman et al. in 1987 [23]. Although researchers have not synthesized large graphyne structures, graphdiyne films and graphdiyne tubes have been already obtained [24,25]. Graphyne consists of planar carbon sheets containing sp and sp2 bonds [26–28], which can be described as the big hexagonal joined together by the acetylenic linkages (C—C≡ C—C) rather than the C—C= C—C in graphene. Accordingly, four different types of graphyne, namely α-, β-, γ-and 6,6,12-graphynes have been identified [29–34]. Among them, γ-graphyne attains better electrical conduction due to its direct band gap [34,35]. Due to large pores in the sheet of γ-graphyne, it is believed to be a promising hydrogen storage material. Several recent reports suggest that metal atom decorated γ-graphyne can adsorb hydrogen with a high gravimetric density [36–41]. However, to the best of our knowledge, there has been no study in hydrogen storage properties of Mg-decorated γ-graphyne.

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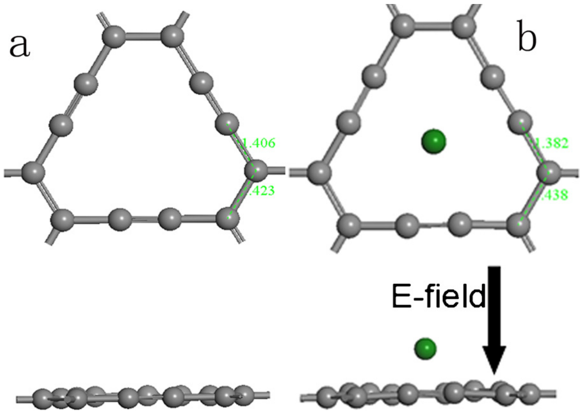

Fig. 1. (a) Optimization of graphyne. (b) Mg-decorated γ-graphyne. Dark gray balls are carbon atoms. Black arrows indicate the direction of the electric field.

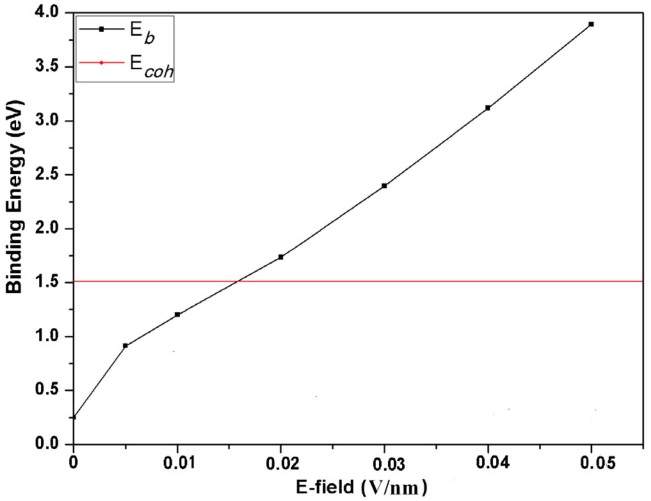

Fig. 3. The binding energy (E_b) of the Mg atom on the graphyne layers in the presence of an external electric field. The cohesive energy (E_{coh}) value of the Mg metal bulk (red line) is also presented for comparison purposes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In this work, for the first time, we use an external electric field to prevent aggregation of Mg atoms on γ-graphyne using density functional theory (DFT) calculations. We also investigate hydrogen storage properties of the processed Mg-G with electric field (F = 0.05 V/nm). Each Mg atom can adsorb up 10H_2 molecules, with average adsorption energies of 0.28 eV/H_2. The hydrogen storage capacities is 10.64 wt%. The hydrogen storage capacity largely surpasses the target of DOE, and the results suggest that γ-graphyne is a potential material for hydrogen storage.

2. Computational framework

All geometry optimizations are carried out using DFT calculations within the local density approximation (LDA) as implemented in the DMol^3 package [42,43] with Perdew-Wang (PWC) functional for exchange-correlation energy. Previous studies have shown that LDA can predict the physisorption energies of H_2 on the surface of carbon nanotubes and graphite accurately [44,45] and can be suitable for charged carbon nanostructures with electric fields [46,47]. The dispersion-corrected DFT (DFT-D) [48,49] scheme put forward by Ortmann, Bechstedt, and Schmidt (OBS) [50] is also used in the calculations for Mg-G and nH_2/(Mg-G) systems. A double numerical plus polarization (DNP) is selected as the basis set. The DNP basis set corresponds to a double-DFT semi-core pseudo potentials (DSPP) treatment is employed as the core treatment for relativistic effects. It has been known that the numerical basis sets implemented in DMol^3 code are more complete than the traditional Gaussian functions, thereby minimizing or even eliminating basis set superposition error (BSSE) [51]. As a result, DMol^3 code does not contain BSSE correction procedure [52,53] and BSSE effect will not be considered in this study. The *k*-point is set to 12 × 12 × 12, and all atoms are allowed to relax. The global orbital cutoff 5.2 Å is set in the spin-unrestricted calculations. To avoid the inter layer interaction between neighboring layers, a vacuum space of 20 Å is applied along the direction perpendicular to the γ-graphyne sheet. Charge transfer is calculated using the Mulliken charge analysis method. The electric field is downward and perpendicular to the γ-graphyne layer in *z* direction, as shown in Fig. 1(b). The adsorption energy of Mg on γ-graphyne is determined by the following function,

$$E_{ad}(\mathrm{Mg}) = E(\mathrm{Mg\text{-}G}) - E(\mathrm{Mg}) - E(\mathrm{G}) \quad (1)$$

where E_{ad}(Mg-G), E(Mg) and E(G) are total energies of Mg decorated γ-graphyne after fully relaxation, an isolated Mg atom and γ-graphyne sheet, respectively.

For the case of Mg adsorbed on γ-graphyne sheets under the intensity of field F,

$$E_{Fad}(\mathrm{Mg}) = E_F(\mathrm{Mg\text{-}G}) - E_F(\mathrm{Mg}) - E_F(\mathrm{G}) \quad (2)$$

where the subscript “F” indicates the energy of fragments is obtained in the presence of the external F.

The average adsorption energy of H_2 on Mg-G is defined by

$$E_{ad}[H_2] = [nH_2/E_F(\mathrm{Mg\text{-}G}) - E_F(\mathrm{Mg\text{-}G}) - nE_F(H_2)]/n, \quad (3)$$

where *n* is the number of H_2 molecules adsorbed.

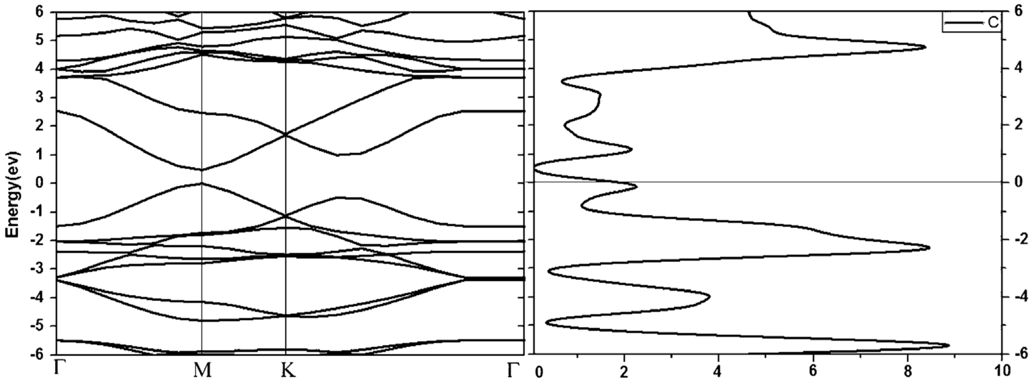

Fig. 2. The electronic band structure and partial density of states (PDOS) of the γ-graphyne. The Fermi energy is set to zero.