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Hydrogen storage using Na-decorated graphyne and its boron nitride analog

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ABSTRACT

Na-decorated single- and double-sided graphyne and their BN analogs have been proposed to be promising hydrogen storage candidates. The structural stability of metal/graphyne and metal/BN and the metal adsorption sites on the layers were studied in virtue of density-functional theory calculations. Hydrogen storage behaviors on the complexes were investigated. The calculated results demonstrated that each Na atom could attach at most three hydrogen molecules without any dissociation of molecule structures. For Na-decorated double-sided graphyne and BN analog, the hydrogen storage capacities could reach to 5.98 and 5.84 wt%, with the average adsorption energies of −0.25 and −0.17 eV/H_2, respectively. The hydrogen binding mechanisms are unrevealed by analyzing the charge transfer and density of states of the systems.

Introduction

Hydrogen is widely accepted as a renewable clean energy and an ideal substitution of traditional carbon based fossil fuels. However, the technical challenge of hydrogen application is the lack of safe and efficient hydrogen carriers [1–4]. Since graphene experimental breakthrough in 2004 [5], it has led to an extraordinary amount of interests due to its unique electronic structure and excellent physical and chemical properties [5,6], and in particular, graphene has been demonstrated to exhibits fantastic hydrogen storage capacity. Elias et al. successfully fabricated graphane by placing the graphene sheet into hydrogen atom atmosphere [7]. Although the transition from graphene to graphane resulted in an extremely high hydrogen storage capacity, the strong chemical bond between hydrogen atom and carbon atom would lead to a great difficulty of the hydrogen desorption process. In comparison to fullerene, carbon nanotube and nanorope, graphene has relatively large surface and both sides can be employed to store hydrogen molecules.

Considering the obvious advantage of two dimensional nanostructures using as gas tank and energy storage, a novel allotropic form of carbon – graphyne is expected to possess an excellent performance on hydrogen storage [8]. In 1987, Baughman group predicted the possibility of graphyne and has successfully synthesized graphdiyne at the first time [9]. In the light-weight nano materials area, structures formed by carbon and boron nitride are quiet popular. There are 0-D structures like fullerene and boron nitride nanocage [10], 1-D structures like carbon nanotube [11,12] and boron nitride nanotube [13], 2-D structures like graphene [14] and boron nitride nanosheet

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[15]. The prediction of the possibility and stability of graphyne inspires the possible existence of the structure of graphyne-like boron nitride layer (BN-yne). In this contribution, Na-decorated graphyne and BN-yne are designed as hydrogen storage materials. The binding energy between Na and the matrixes were calculated using density-functional theory (DFT) method. We found that each metal atom can catch up three hydrogen molecules without any dissociation. For Na-decorated double-sided graphyne and BN-yne, the hydrogen storage capacities are 5.98 and 5.84 wt%, with average adsorption energies of −0.25 and −0.17 eV/H_2, respectively. The optimized geometries and electronic structures of hydrogen molecules adsorption on storage candidates were also obtained.

Modeling and simulation details

All computations were carried out using spin-polarized DFT calculations as implemented in the DMol^3 package which is widely used for calculations of adsorption properties of carbon nano materials [16]. For the calculation of exchange-correlation potential, local density approximation (LDA) and generalized gradient approximation (GGA) functionals are commonly employed. In this paper, the exchange-correlation potential of electrons is treated using LDA with Perdew-Wang (PWC) functional [17]. K-point for calculation of total energy is set to 12 × 12 × 1 which is large enough that the difference of total energy calculated by larger sets of k-points is negligible. DFT semi core pseudopot is selected to be employed as core treatment and DNP is opted to be the basis set. The global orbital cutoff is set to 5.2 Å. The Monkhorst-pack grid parameter of density of state is 16 × 16 × 1.

We firstly optimize the two dimensional structure of graphyne showed in Fig. 1(a), getting lattice constant of 6.86 Å which is in consistent with previous theoretical results [18,19]. The vacuum region in the direction perpendicular to the plane is chosen to be 20 Å to minimize the interaction of artificial intercells. Due to the fact that when B and N atoms are doped into carbon nanostructures such as graphene and graphdiyne, they tend to occupy the neighboring sites, we use BN pairs to dope with two adjacent carbon atoms of graphyne and obtain the optimized structure of BN-yne, shown in Fig. 1(b).

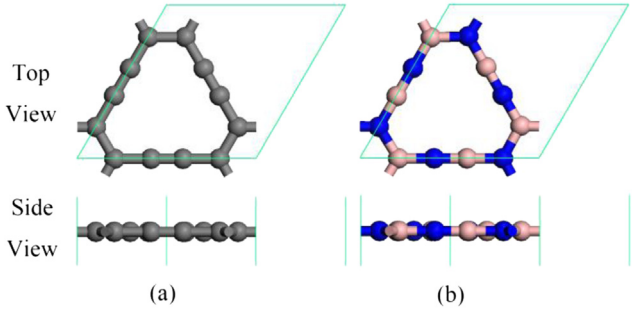

Fig. 1 – (a) and (b) depict optimized geometries of graphyne and BN-yne, respectively. Dark gray balls are carbon atoms. Blue and pink balls denote nitrogen and boron atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Results and discussions

Hydrogen adsorption of Na-decorated single- and double-sided graphyne

Fig. 1(a) depicts the optimized structure of (1 × 1) graphyne unit cell where all atoms are fully relaxed without any constrains. The calculated lattice constant (6.86 Å) is in good agreement with previous DFT calculations [20]. The bond length of carbon hexagonal ring is 1.42 Å, in line with carbon bond length of graphene. Different initial adsorption sites of Na on graphyne are considered, including hexagonal hollow site, triangle hollow site, and the site above acetylenic bond. The adsorption energy of Na on graphyne (or BN-yne) E_{ad} [Na] can be calculated by,

$$E_{ad}\,[\mathrm{Na}] = \{E\,[i\mathrm{Na/G(or\ BN\text{-}yne)}] - iE\,[\mathrm{Na}] - E\,[\mathrm{G(or\ BN\text{-}yne)}]\}/i, \quad (1)$$

where E [iNa/G(or BN-yne)] denotes the total energy of Na adsorption on graphyne (or BN-yne) after relaxation. E [Na] and E [G(or BN-yne)] are the total energies of an isolated sodium atom and pristine graphyne or BN-yne. i equals to 1 and 2 denotes the configurations of Na-decorated single and double sides of graphyne, respectively. Thus, a negative result implies that the spontaneous process of Na adsorption. Similar as the case of other alkali metal adsorption on graphyne [21–24], we find that the site above the hollow site of triangle linkage consisted with acetylenic bond is the most favorable adsorption site for Na on graphyne with the lowest adsorption energy of −2.37 eV. The binding energy between Na atom and graphyne (or BN-yne) is defined as,

$$E_b\,[\mathrm{Na}] = \{iE\,[\mathrm{Na}] + E'\,[\mathrm{G\ (or\ BN\text{-}yne)}] - E\,[i\mathrm{Na/G\ (or\ BN\text{-}yne)}]\}/i, \quad (2)$$

where E' [G (or BN-yne)] is the total energy of pristine graphyne or BN-yne after the attachment of Na atoms. The geometries of Na/graphyne and charges of Na are shown in Fig. 2(a). Transition state calculation shows that the diffusion

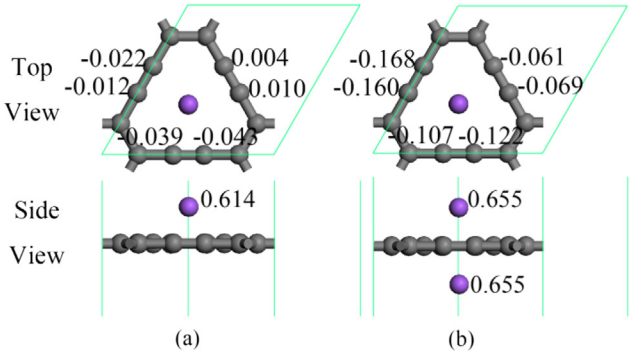

Fig. 2 – Optimization of Na-decorated single and double-sided graphyne. Dark gray and purple balls denote carbon and Na atoms. Charges of Na and its six nearest carbon atoms are shown in this figure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)