



Research paper

Ab initio insight into graphene nanofibers to destabilize hydrazine borane for hydrogen release



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ABSTRACT

We report the potential destabilizing effects of graphene nanofibers on the hydrogen release property of hydrazine borane via state-of-the-art ab initio calculations for the first time. Interactions of a hydrazine borane cluster with two types of graphene patch edges which exist abundantly in our synthesized graphene nanofibers have been investigated. It is found that both zigzag and armchair edges can greatly weaken the H-host bonds (especially the middle N–H bond) of hydrazine borane. The dramatic decrease in hydrogen removal energy is caused by the strong interaction between hydrazine borane and the graphene patch edges concerning the electronic charge density redistribution.

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1. Introduction

The availability of a sustainable energy resource has become one of the world's biggest challenges with the development of society and the increasingly larger supply-demand gap of fossil fuels in the long run. Production and storage of clean or green fuels are being addressed and are at the center of attention for many scientists and engineers. Hydrogen fuel is one example discussed widely as a possible solution to the problems we are facing, although at the moment, many hurdles remain to be overcome before a realistic implementation becomes feasible. Besides the unsolved issue of large-scale hydrogen production via renewable energy, requirement of more reliable and economic materials and methods for hydrogen storage is the second biggest technical bottleneck to realize the green hydrogen economy [1–5].

As a kind of inorganic hydride material, Hydrazine borane ($N_2H_4BH_3$) possesses hydrogen capacity as high as 15.4 wt%, which is a promising candidate for hydrogen storage applications [6–8]. For the direct thermal decomposition of hydrazine borane (HB in abbreviation), there had been no known very effective metal-free

destabilizer reported yet to improve its hydrogen desorption. Carbon based nanomaterials, which generally have large specific surface areas, have been studied in other hydrogen storage systems to enhance the hydrogen sorption [9–11]. While in this letter, using *ab initio* atomistic modeling, we have theoretically explored the potential destabilizing effects of graphene nanofibers on the hydrogen release of hydrazine borane for the first time.

2. Methodology

We have performed state-of-the-art density functional theory [12,13] calculations using the projector augmented wave (PAW) method [14], which is implemented in the Vienna Ab initio Simulation Package [15,16]. The generalized gradient approximation (PW91) [17] has been used. Geometry optimization has been fully done by minimizing the total energy of the supercell system with a conjugate gradient algorithm converged to less than 0.00001 eV. We have employed a plane wave basis set with an energy cutoff of 520 eV to describe the electronic wave function. Visualization for Electronic and Structural Analysis [18] has been used to visualize and analyze the structures. The supercell of $15 \text{ \AA} \times 20 \text{ \AA} \times 10 \text{ \AA}$ has been tested for convergence and been used. For the k-point, only a single Gamma-point is required. The PAW potentials with

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the valence states 2s2p for C, 2s2p for B, 2s2p for N and 1s for H have been employed in the work. The results reported here have been successfully tested for convergence in terms of the cutoff energy, k-point samplings of the Brillouin Zone, etc. During the calculation of hydrogen removal energies, the ground state energy of a hydrogen atom has been employed instead of the total energy of a hydrogen molecule (thus what should be noted is, there would occur a data difference with respect to the bonding energy of two hydrogen atoms if the total energy of a hydrogen molecule is used). The hydrogen removal energy has been calculated considering the following equation (All the energies are the ground state values):

$$\Delta E = E(\text{the system after one hydrogen atom is removed}) + E(\text{H}) - E(\text{the system before hydrogen removal}).$$

The differential electron densities have been analyzed by solving the iterative problem through a self-consistent way using the Kohn-Sham ansatz:

$$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \quad (1)$$

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (2)$$

$$V_{\text{eff}} = V_{\text{ext}} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho(\mathbf{r})} \quad (3)$$

$$\Delta \rho = \rho(\text{G} + \text{HB}) - \rho(\text{G}) - \rho(\text{HB}) \quad (4)$$

In (4), the $\rho(\text{G} + \text{HB})$ stands for the charge density of the interacting system (graphene patch layer + hydrazine borane) after self-consistent calculations; the $\rho(\text{G})$ and $\rho(\text{HB})$ mean the charge densities of the isolated graphene patch layer and hydrazine borane respectively (keeping the same supercell size and respective coordinates as they are in the interacting system).

The Bader charge analysis [19–21] has been done to analyze the atomic charge states in the investigated materials.

3. Results and discussion

Experimentally, we have already synthesized graphene nanofibers using Fe nanoparticles as growth catalyst (the experimental synthesis method and the morphology of the synthesized graphene nanofibers are placed in the [Supplementary Material that includes Fig. S1](#)). The noticeable feature is that the synthesized sample contains both the planar graphene nanofibers (PGNF) and the helical graphene nanofibers (HGNF), which is due to the usage of Fe nanoparticles of non-uniform shape as catalyst during the growth process. The growth of HGNF is due to the uniform distribution of faceted or polygonal shape catalyst particles whereas the growth of PGNF is due to spherical shape catalyst particles. While, it should be noted that both types of GNFs consist of stacked graphene patch layers although they differ in the way of stacking, which would cause the existence of large amounts of graphene edges at the surface of GNFs. Thus in this work, from the perspective of atomistic modeling we have focused on and investigated the effects of graphene patch edges on hydrogen release of hydrazine borane, which would help to predict the potential effects of these graphene nanofibers. Since the graphene edges can have two types (zigzag or armchair) and the edge structures and properties (such as electronic conductivity, etc.) of the two types are different, here in this study we have considered both types. Different local charge densities and electronic structures are also expected due to different atomic arrangements of the edge carbon atoms.

To avoid the chemical effect of some heterogeneous species such as H, O and OH (the FTIR study of GNFs didn't reveal the sig-

nature of these species), we have employed a graphene patch as our model by fixing some of its edge atoms (represented by the circles "filled" with gray color in [Fig. 1](#)) to simulate their bonding with neighboring carbon atoms further inside the graphene nanofiber restricting their movement. [Fig. 1](#) gives the ground state equilibrium structures of the graphene patch interacting with hydrazine borane cluster and its hydrogen removal products when we consider the effects of graphene zigzag edge. From [Fig. 1\(a\)](#) it can be seen that the hydrazine borane cluster stays far away from the zigzag edge after geometry optimization. When one hydrogen atom is removed from the boron site, after relaxation it can be seen from [Fig. 1\(b\)](#) that the boron atom has interacted with the most nearby carbon atom with a bond distance of 1.60 Å. The evident "pull-out" of the involving carbon atom and resulting distortion of the hexagon also reveals this. [Fig. 1\(c\)](#) shows the case when one hydrogen atom is removed from the middle nitrogen site of hydrazine borane. Surprisingly, after one hydrogen is removed from the middle nitrogen site, the boron atom also loses one hydrogen atom which finally bonds with one of the carbon atoms. Examination of the bond lengths reveals that the nearest C–N distance is 1.54 Å and the N–B bond length decreases to 1.54 Å compared with 1.62 Å of the case before hydrogen removal. [Fig. 1\(d\)](#) is the case of hydrogen removal from the terminal nitrogen site of hydrazine borane. Also interestingly, the removal has led to the leaving of one hydrogen atom from the middle nitrogen site. The bond length of N–N has found to decrease from the pristine 1.45 Å to 1.26 Å, which is the signature of the double bond forming.

[Fig. 2](#) illustrates the cases of hydrazine borane located near an armchair edge of the modeled graphene patch. [Fig. 2\(a\)](#) shows the relaxed configuration before any hydrogen removal has taken place. After one hydrogen atom is removed from the boron site of hydrazine borane, the relaxed configuration is shown in [Fig. 2\(b\)](#). The boron atom has bonded with the most nearby carbon atom with the length of 1.57 Å; what is interesting is that the removal leads to the leaving of another hydrogen atom from the boron site (also bonded with one carbon atom), which has helped to form the "hexagonal" shape of the local lattice together with the boron atom. The case of hydrogen removal from the middle nitrogen site of hydrazine borane at the graphene armchair edge is even more interesting. It can be shown in [Fig. 2\(c\)](#) that the removal has even caused the leaving of another two hydrogen atoms: one from the boron site and the other from the terminal nitrogen site. Both of two hydrogen atoms have bonded with carbon. The boron atom has also interacted with the most nearby carbon atom with a distance of 1.62 Å. [Fig. 2\(d\)](#) shows the equilibrium configuration after one hydrogen atom is removed from the terminal nitrogen site of hydrazine borane. Similar to the case in [Fig. 1\(d\)](#), there also occurs the leaving of one hydrogen atom from the middle nitrogen site and the great decrease of N–N bond length to 1.25 Å.

The hydrogen removal energy can be used as a rough indicator of possibility and reaction temperature of hydrogen desorption [22,23]. In order to predict or estimate the potential effects of graphene nanofibers, we have calculated the single hydrogen removal energies based on the configurations displayed in the above [Figs. 1 and 2](#). [Fig. 3](#) shows the results compared with the case of pure hydrazine borane cluster (without support of carbon edges). It can be obviously seen that the graphene edges can help to decrease the hydrogen removal energy of hydrazine borane greatly regardless of the type of edges. Especially for the middle nitrogen site, it can be regarded that the graphene edges have weakened the middle N–H bond of hydrazine borane most (the smallest hydrogen removal energy value of –0.52 eV for zigzag case and that of –1.60 eV for armchair case, respectively). We have also performed some test calculations in which the H-saturated carbon atoms replaced the fixed atoms in pure carbon sheet model. The

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