Charge-controlled switchable H₂ storage on conductive borophene nanosheet

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Abstract

Conductive borophene nanostructures are proposed as an excellent candidate material for charge-controlled switchable H₂ storage. Based on density functional theory calculations, we investigate the H₂ adsorption on the charged borophene nanosheet. It is found that the adsorption energies of H₂ on either positively or negatively charged borophene nanosheets are dramatically enhanced in compared with the neutral material. Charge modulation strategies therefore offer the potential for spontaneous, controllable H₂ storage and release. Moreover, the positive or negative charging of borophene nanosheets can in principle achieve H₂ storage capacities of 6.5 wt%. These results could provide new insights in searching for materials with exceptionally high H₂ storage capacity.

Keywords: H₂ storage; Charge-modulated; DFT calculations; Adsorption energy; Borophene.

Introduction

Hydrogen with renewable nature and high energy content of hydrogen has already been widely anticipated as a predominant alternative to fossil fuels. However, a safe, economically and technically viable H₂ storage media is the most demanding and challenging requirement for realizing a hydrogen economy[1-3], which highlights the need for exploring ideal hydrogen storage methods. The U.S. Department of Energy (DOE) sets up H₂ storage standards of 5.5 wt% in gravimetric capacity at an temperature between -40 and 60 °C and a maximum delivery pressure of 100 atm[4].

Although several classes of nanostructures have been developed for H₂ storage, such as nanostructures, molecular complexes and metal hydrides, these materials still suffer from insufficient storage capacity, poor reversibility and high dehydrogenation temperatures[5,6]. The emerging 2D materials[7-9] (graphene, BN and phosphorene) are considered to shed a light for developing the next-generation hydrogen storage materials due to their large surface to volume ratio. However, weak H₂ adsorption enthalpies of these structures significantly prevent their application of being feasible H₂ storage materials. It has been reported that alkali-earth metal or transition metals decorated 2D sheets could increase H₂ adsorption energy[10-14]. For example, a structure where Li atoms capped onto the fullerene surface was stable and stored up to 120 hydrogen atoms with a binding energy of 0.075 eV/H₂. However, metal atoms tend to cluster, resulting in degradation in performance[15].

To deal with this issue, Zhou et al.[16] proposed a novel strategy of reversible H₂ storage. Density functional theory (DFT) results proved the gravimetric density of adsorbed H₂ could reach 7.5 wt% via applying an external field to BN sheet. Moreover, when the applied electric field was removed from BN sheet, the system went back to its original state and H₂ molecules could desorb from BN sheet. However, the electric field strength in this study is around 23000 MVm⁻¹, which was too large for experimental realization. On the other hand, researchers also found that when extra charges were injected into adsorbents, the gas adsorption capacity of this adsorbents could be extremely enhanced[17-21]. Notably, the kinetics of gas adsorption and release could be modulated by tuning charge density, yielding a

controlled adsorption and desorption process. Until now, various materials have been developed and explored for charge-controlled H₂ storage[17-21]. B-doped graphene has been proposed as an excellent charge-modulated H₂ storage material. For example, the positively charged BC₅ nanosheet could have a high H₂ storage capacity of 5.3 wt%. Moreover, the calculation results showed that H₂ storage and release occurred spontaneously without any energy barrier when extra electrons were injected or removed[17]. C₂N, successfully synthesized by a bottom-up wet-chemical approach[22], has also been discovered to be an efficient charge-modulated H₂ storage material. The investigation showed that the negatively charged C₂N could have an impressively high H₂ adsorption capacity with gravimetric density of 10.5 wt%[21].

Very recently, different types of borophene nanostructures have been successfully synthesized in experiment[23,24]. Exactly, both β_{12} sheet and χ_3 sheet are planar borophene nanosheets that have been recently grown successfully on a single-crystal Ag(1 1 1) surface[23]. Another borophene structure, denoted as a striped borophene structure with out of plane buckling, which has been synthesized experimentally by Mannix et al.[24] In addition, previous investigations have indicated that these borophene structures exhibit metallicity and high electronic conductivity[23-25]. Due to its exceptional electronic property, borophene has been applied in various fields, such as lithium-ion batteries[26,27], hydrogen detection and storage[28-31]. Recently, investigations of gas capture properties on negatively charged borophene by Tan et al. have indicated its great potential in CO₂ capture[31]. The high electronic conductivity of borophene and its great potentials in gas storage inspired us to explore if this material could also be exploited for charged-controlled switchable H₂ storage.

To prove the above hypothesis, DFT calculations were adopted to systematically investigate H₂ adsorption properties on neutral, positively and negatively charged borophene nanosheet from both thermodynamic and kinetic points of view. Here, we chose the striped borophene nanosheet as an example due to its densest structure, which could provide more H₂ adsorption sites. The results show that the H₂ molecules adsorption strength can be significantly enhanced on either positively or negatively

charged striped borophene. In comparison with other H₂ capture approaches, H₂ capture and release process on the charged striped borophene nanosheets, which could occur spontaneously without any energy barrier, could be simply controlled by turning on/off charges on striped borophene nanosheet. At saturation H₂ coverage, the capacities of positively and negatively charged striped borophene could reach 6.5 wt%. Our investigation will provide valuable directions for experimentally designing practical, controllable and high H₂ storage capacity materials.

Model and Method

All simulations were based on DFT method implemented in DMol³ code[32] using generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) for exchange and correlation potential function[33,34]. Double numerical plus polarization (DNP) was adopted for the basis set. A DFT+D method of which D indicates dispersion with Grimme scheme[35] was used to describe the van der Waals (vdW) interactions between striped borophene and H₂ molecules. Here, a (2 × 4) supercell structure with periodic boundary conditions in the *x-y* directions (Fig. 1(a)) was employed to model the striped borophene and the vacuum space was larger than 20 Å along the *z* direction during simulations. In addition, the atomic forces were smaller than 0.001 Ha/Å, and the convergence tolerances were around 10⁻⁵ Ha (1 Ha = 27.2114 eV) during geometric optimizations. The k-point mesh size was 6 × 6 × 1 for Brillouin zone integration for all calculations[36]. The adsorption energy[31,37] of H₂ on striped borophene was obtained via:

$$E_{ad} = (E_{borophene+H_2} - E_{borophene} - nE_{H_2}) / n$$

where $E_{adsorbent+gas}$, $E_{adsorbent}$ were the total energies of adsorbent with and without H₂ molecules, E_{gas} was the total energy of isolated H₂ molecules, *n* was the number of H₂ molecules. Based on this definition, a larger absolute value of adsorption energy showed that the striped borophene nanosheet interacts more strongly with H₂ molecules. It should be noted that the conventional simulation approaches to charge-controlled switchable gas capture could introduce inevitable artifacts because of incomplete convergence of interlayer interactions across periodic boundaries. Here, we used the correction procedure proposed by Bal et al.[38] to obtain fully converged

adsorption of H₂ molecules.

Results and Discussions

Geometric and Electric structures of the striped sheet of Borophene

Because striped borophene structure is densest structure compared with other borophene structures, which could provide more adsorption sites and contribute to higher H₂ storage capacity. Therefore, we focus on studying H₂ storage capacity of striped borophene structure. The optimized borophene structure with a unit cell of $a = 1.601 \text{ \AA}$ and $b = 2.851 \text{ \AA}$ is presented in Fig. 1a. The calculated band structure indicates that this striped borophene structure (Fig. 1b), which demonstrates that this striped borophene structure is metallic (band gap is 0 eV). These results are well in agreement with the reported experimental and theoretical results[24,39]. The good conductivity could make the striped borophene possible to be a charged controlled H₂ storage material by injecting extra electrons.

Fig. 1 (a) Top and side configurations of the lowest-energy structure of (2×4) striped borophene nanostructure. The unit cell of striped borophene nanostructure is labeled with dashed lines. (b) The calculated band structure of (2×4) striped borophene sheet.

Adsorption of single H₂ molecule on neutral and charged striped borophene nanosheet

Firstly, we investigate adsorption property of a H₂ molecule on neutral and charged striped borophene nanosheet. Fig. 2 represents the most stable configurations of one

H₂ molecule absorbed on the boron atom of neutral, 1.4 e positively and 1.5 e⁻ negatively charged striped borophene surface. The H₂ molecule adsorbs perpendicularly to neutral striped borophene surface with a distance of 2.784 Å (Fig. 2a). The H-H bond length is 0.753 Å. In addition, Mulliken population analysis shows that electron transfer between H₂ molecule and neutral striped borophene is 0.008 e⁻. The adsorption energy of H₂ molecule on neutral striped borophene sheet is -0.057 eV, suggesting the weak interactions between the neutral striped borophene sheet and H₂ molecule.

After injecting extra charges into the striped borophene sheet, the interactions between H₂ molecule and the charged surface are greatly enhanced, as shown in Fig. 2b and 2c. For 1.4 e positively charged striped borophene sheet (Fig. 2b and Fig. S1), the distance between H₂ molecule and adsorbent surface is shortened to 1.915 Å when the H-H bond length is elongated to 0.782 Å. Mulliken population analysis shows that charge transfer from positively charged striped borophene surface to H₂ molecule is increased to 0.175 e. Moreover, it should be noted that the upper H atom of H₂ molecule is positive (0.257 e) and the lower one is negative (0.082 e⁻), demonstrating that the extra positive charges polarize H₂ molecule. The polarized H₂ molecule interacts strongly with the positively charged striped borophene sheet, contributing to an increased H₂ adsorption energy of -0.231 eV. In terms of 1.5 e⁻ negatively charged striped borophene sheet (Fig. 2c and Fig. S2), the distance between H₂ molecule and adsorbent surface is shortened to 2.131 Å and the H-H bond length is lengthened to 0.778 Å. Mulliken population analysis demonstrates that the electron transfer between negatively charged striped borophene and H₂ molecule are 0.091 e⁻. The charges of upper and lower H atoms are 0.272 e⁻ and 0.181 e, respectively. Similarly, extra negative charges could polarize H₂ molecule, which contributes to the improved interactions (-0.236 eV) between H₂ molecule and striped borophene sheet. Additionally, the total charge density distributions of a single H₂ molecule adsorbed on the neutral, 1.4 e and 1.5 e⁻ charged borophene surfaces are also depicted to give better understanding of H₂ adsorption properties (Fig. S3). It is obvious that a new bond between the B atom of positively or negatively charged borophene and the H

atom of H₂ molecule is formed (Fig. S3b and 3c). This is significantly different from the case of H₂ on the neutral borophene (Fig. S3a), which could well explain why H₂ molecule has a strong interaction with positively or negatively charged borophene.

Fig. 2 The most stable configurations of a H₂ molecule on the (a) neutral, (b) 1.4 e positively and (c) 1.5 e⁻ negatively charged striped borophene sheet.

The recyclability of the material for H₂ storage is of great importance for its practical application. Thereby, we study the kinetic process of H₂ adsorption/desorption on charged striped borophene nanosheet by computing the adsorption energy change of H₂ molecule when the extra charges are injected or removed, as shown in Fig. 3-4 and Fig. S1-2. For the H₂ adsorption process on positively charged striped borophene (Fig. 3a), we start the simulation with the lowest-energy configuration of H₂ molecule on neutral striped borophene nanosheet. Then, 1.4 extra charges are introduced into the neutral striped borophene. Fig. 3a depicts the change of adsorption energy when the system relaxes to 1.4 e positively charged optimization state. It is obvious that H₂ adsorption strength on the positively charged striped borophene could be greatly enhanced with an adsorption energy of -0.231 eV. According to the calculated adsorption energies, it is demonstrated that the adsorption process is spontaneous and exothermic by 0.113 eV. Fig. 3b depicts H₂ desorption process from striped borophene nanosheet after removing 1.4 extra charges. The system is allowed to relax to the stable state when 1.4 extra charges are extracted

from this surface. It is found that H₂ molecule spontaneously returns to the weak bond state with a weak interaction of -0.057 eV and desorbs from striped borophene. This desorption process is exothermic by 0.095 eV without any energy barrier.

For H₂ adsorption process on negatively charged striped borophene, Fig. 4a shows the initial and lowest energy configurations of H₂ adsorption on 1.5 e⁻ charged striped borophene nanosheet. When 1.5 extra electrons are added to this material and the system relaxes to the optimized state. It is discovered that the interactions between H₂ molecules and striped borophene are boosted significantly. This process is spontaneous and exothermic by 0.107 eV based on the computed adsorption energy change. The H₂ desorption process by removing 1.5 e⁻ negative charges is depicted Fig. 4b. 1.5 electrons are removed from the striped borophene and the system relaxes to the stable state, resulting in weak interactions between the striped borophene and H₂ molecules. This desorption process is also demonstrated to be exothermic by 0.008 eV, indicating that H₂ molecule could spontaneously desorb from the striped borophene without any energy barrier. Based on the above-mentioned discussions, H₂ storage and release on the striped borophene nanosheet could be easily controlled by tuning its charge state, demonstrating that this striped borophene monolayer could be a great candidate for charge-controlled switchable H₂ capture.

Fig. 3 Adsorption energy change of (a) H₂ capture process on striped borophene by injecting 1.4 extra charges; (b) H₂ release process on striped borophene by removing 1.4 extra charges.

Fig. 4 Adsorption energy change of (a) H₂ adsorption process on striped borophene by injecting 1.5 extra electrons; (b) H₂ release process on striped borophene by removing 1.5 extra electrons.

Moreover, we also investigate the influence of charge density on H₂ adsorption behaviors on charged striped borophene. Herein, the charge densities of striped borophene is calculated by $\rho = Q/S$ (ρ , Q and S represent the charge density, total charge and the surface area of (2×4) striped borophene sheet, respectively). The adsorption energy of H₂ molecule, the induced moment of H₂ molecule, the H-H bond length and the electron transfer between H₂ molecule and striped borophene nanosheet are depicted as a function of charge density in Fig. 5 and Fig. 6. It could be found that the dipole moment (Fig. 5b and 6b) and the H-H bond length (Fig. 5c and 6c) significantly rise with increasing positive or negative charge densities, which is attributed to the improved electric field generated around charged striped borophene surface. The Mulliken population analysis indicates that the electron transfer number increases with increasing positive or negative charge densities, as depicted in Fig. 5d and Fig. 6d. In general, the adsorption energy (Fig. 5a and 6a) of H₂ molecule on positively or negatively charged striped borophene surface is dramatically increased with the increasing charge densities. It is noted that the adsorption energies of one H₂ molecule on 1.4 e positively charged and 1.5 e⁻ negatively charged striped borophene surface are -0.231 eV and -0.236 eV, respectively, whose absolute values are larger than normal H₂ adsorption energy (0.1 eV ~ 0.2 eV),¹⁶ demonstrating that positively and negatively charged striped borophene show strong interactions with H₂ and its

potential for charge-controlled H₂ storage.

Fig. 5 (a) H₂ adsorption energy, (b) induced H₂ dipole moment, (c) H-H distance, (d) electron transfer between H₂ molecule and positively charged striped borophene as a function of different positive charge densities.

Fig. 6 (a) H₂ adsorption energy, (b) induced H₂ dipole moment, (c) H-H distance, (d) electron transfer between H₂ molecule and negatively charged striped borophene as a function of different negative charge densities.

H₂ storage capacity of the charged striped borophene nanosheet

In this section, we investigate the H₂ storage capacity on 1.4 e positively and 1.5 e⁻ negatively charged striped borophene nanosheets by calculating the average adsorption energy of H₂ molecules. According to our calculations, it is demonstrated that six H₂ molecules absorbed on the boron atoms of (2 × 4) striped borophene nanosheet are the saturation H₂ storage coverage, as shown in Fig. 7 and Fig. S4-6. The 1.4 e positively or 1.5 e⁻ negatively charged striped borophene could adsorb up to 6 H₂ molecules with average adsorption energies of -0.212 and -0.223 eV, respectively, which are 4 times larger than that on neutral striped borophene surface (-0.053 eV). Then, we calculate the correlation between the average adsorption energies of 6 H₂ molecules with charge states, as depicted in Fig. 8. Obviously, the average H₂ molecules adsorption energy increases from -0.053 eV to -0.220 eV when the charge number is increased from 0 to 1.4 for positively charged striped borophene nanosheet. On the other hand, the average adsorption energy of H₂ molecules increases from -0.053 eV to -0.223 eV when the number of electron is increased from 0 to 1.5 for negatively charged striped borophene nanosheet. Here, we compute the weight percentage of H₂ molecules on the charged striped borophene nanosheet based on the equation of $(m_{\text{H}_2})/(m_{\text{H}_2}+m_{\text{borophene}})$, which could be up to 6.5 wt%. This value exceeds the target (5.5 wt%)⁴ set by DOE, demonstrating that positively and negatively charged striped borophene nanosheets are high-performance H₂ storage materials.

Fig. 7 The side views of most stable configurations of 6 H₂ molecules on (a) neutral, (b) 1.4 e positively and (c) 1.5 e⁻ negatively charged striped borophene, (d) the top view of most stable configurations of 6 H₂ molecules.

Fig. 8 The average adsorption energies of 6 H₂ molecules on positively (a) and negatively (b) charged striped borophene as a function of positive and negative charges.

Conclusions

In summary, we have systematically investigated H₂ storage capacities of positively and negatively charged striped borophene nanosheets through DFT calculations. It is found that the adsorption energies of H₂ molecules on either positively or negatively charged borophene sheets are dramatically increased due to the extra charges. For example, while the adsorption energy of H₂ molecule on the neutral striped borophene nanosheet is only -0.057 eV, the H₂ adsorption energies on 1.4 e positively and 1.5 e⁻ negatively charged striped borophene nanosheets are -0.231 and -0.236 eV, respectively. Moreover, in comparison with other H₂ storage approaches, H₂ storage and release process, which are spontaneously without any energy barrier, could be simply controlled by injecting and removing extra charges. In addition, the calculation results demonstrate that both positively and negatively charged striped borophene monolayers could have a high H₂ storage capacity of 6.5 wt%. This theoretical investigation could not only demonstrate the great potential of striped borophene in H₂ storage but also provide useful guidance for developing electrocatalytically switchable and high-capacity H₂ storage materials.

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