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First-principles Study on the Structure and Hydrogen Storage Properties of Na decorated BN Sheet

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Abstract: *The Na decorated BN sheets have a stable sandwich structure and can be regarded as an excellent hydrogen storage material. With respect to first-principles calculation, the electronic structure, geometric structure, partial density of states, mulliken population and ability of absorbing hydrogen molecules of the Na decorated BN sheet have been investigated. The results show that: (1) The most stable structure is Na atom adsorption on the top of N atom, it has the greatest binding energy. (2) Na decorated BN sheet can adsorb twelve H2 molecules and the average adsorption energy is 0.530 eV/H2. (3) The hydrogen storage rate of Na decorated BN sheet is about 8.943wt%. (4) The adsorbed H2 molecules have polarization phenomenon.*

Keywords: *Adsorption Energy, Geometric And Electronic Structure, Partial Density of States, Mulliken Population*

1.Introductıon

With the intensification of the energy crisis, the search for new alternative energy had become the common research goal of scientists in various countries [1]. Hydrogen (H_2) was widely concerned because of its rich reserves, easy synthesis, clean, non pollution and a series of excellent characteristics. However, the commercial application of hydrogen energy was restricted by the delay in the research of hydrogen storage materials. The ideal hydrogen storage materials must have the following advantages [2]: (1) storage mass density ≥ 6wt%; (2) dynamic performance of H_2 at room temperature (the adsorptive energy of H_2 molecule are between 0.2 and 0.6eV/H_2); (3) adsorb and release hydrogen repeatedly. To achieve the goals, the researchers focused on the study of alloy hydrogen storage materials [3-5], coordination hydride hydrogen storage materials [6-8] and carbon based hydrogen storage materials [9-11] in recent year. As a kind of hydrogen storage material, carbon based materials (carbon nanotubes, grapheme etc.) have the advantages of large surface area, small density and adjustable aperture. However, the hydrogen adsorption rate of pure carbon based materials was very low (~0.06eV/H_2) [12], which was far from the dynamic requirements for the rapid absorption of H_2. Further studies have found that the metal doped or decorated pure carbon based materials could improve the hydrogen adsorption energy. Based on the density functional theory, Seenithurai [13] has studied the hydrogen storage properties of Li-decorated double carbon vacancy graphene (DVG) and this leads to a gravimetric storage capacity of 3.89 wt%, when Li was decorated on both sides of DVG, the gravimetric storage capacity reaches 7.26wt%, the average adsorption energies were 0.23eV/H_2 and 0.26eV/H_2 respectively. Using the first-principles calculations, Qiu et al. [14] have studied the hydrogen storage of calcium-decorated BC_2N sheets doped by Boron or Carbon and found that each Ca atom could adsorb four hydrogen molecules, the average adsorption energy was about 0.3eV/H_2 and the gravimetric storage capacity of Ca decorated BC_2NBC and BC_2NCN could reach 8.36wt% and 8.38wt% respectively. BN sheets have a similar structure with graphene so it has become a kind of nanomaterials with potential for hydrogen storage. Chen et al. [15] have

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calculated the hydrogen storage properties of the transition group elements (Sc, V and Cr) adsorptive defect BN sheets, and it could adsorb three H molecules near the transition atoms, the adsorption energy was between 0.25 eV/H_2 and 0.58eV/H_2. The hydrogen storage properties of Li doped hydrogenated BN sheets have been calculated by Banerjee et al. [16] and the results showed that the hydrogen storage energy was about 0.18-0.3eV/H_2 at 200K, the gravimetric storage capacity was about 6wt%. Venkataramanan et al. [17] calculated the hydrogen storage properties of Ni and Rh doped BN sheets, which could adsorb three H molecules around the metal atoms, the adsorption energy of H molecules were 0.739eV/H_2 and 0.692eV/H_2 respectively.

The geometric structure, electronic structure and hydrogen storage property of Na decorated BN sheet have been studied systematically by the first principles method based on density functional theory in this paper. The results showed that Na atoms can be stably adsorbed above the top of N atom, Na decorated BN sheet can adsorb 12 hydrogen molecules and the average adsorption energy reached 0.530 eV/H_2, the hydrogen storage rate of Na decorated BN sheet can reach 8.943wt%.

2. Materials and methods

The calculation was performed by DMol3 codes based on Density Functional Theory (DFT). The exchange-correlation interaction between electrons was described by generalized gradient approximation (GGA) and Becke-threeparameter Lee-Yang-Parr functional (B3LYP). All positions of the atoms were relaxed such that the force on each atom was less than 0.005eV/nm. The energy minimization was done with the convergence to tolerance energy of 3.0×10-4eV/atom. SCF tolerance was less than 3×10-5eV/atom. The Brillouin zone was sampled using 3×3×1 Monkhorst-Pack mesh of special k-points.

The binding energy between Na atoms and BN sheet (E_b) and the average adsorption energy of H_2 molecules (E_{ab}) were defined as follows:

$$E_b = E_{\text{BN}} + E_{\text{Na}} - E_{\text{Na-BN}} \quad (1)$$

$$E_{ab} = \left(E_{\text{Na-BN}} + nE_{\text{H}_2} - E_{\text{Na-BN}+n\text{H}_2} \right) / n \quad (2)$$

where n was the number of H_2 molecule, $E_{Na\text{-}BN}$ was the total energy o the Na-BN sheet and $E_{Na\text{-}BN+nH2}$ was the total energy of the Na-BN+$n$$H_2$ system. E_{H2} was the energy of the single H_2 molecule and E_{Na} was the energy of isolated Na atom. E_{BN} was the total energy of pure BN sheet.

3. Results and dıscussıons

3.1. Geometric Structure, Electronic Structure and Binding Energy

A 3×3×1 supercell containing nine B atoms and nine N atoms with periodic boundary conditions along the *x* and *y* axes were used to model the BN sheet. A 2nm vacuum layer was built in the *z* direction in order to eliminate layer-to-layer effects. After optimizing the structure of BN sheet, the B-N bond length was 0.142 nm, it differs from the result of literature [18] (0.144 nm) by 1.4%. Na atom could adsorb on the bridge site (B), hollow site (H), B top site (T_B) and N top site (T_N) respectively. The binding energy between Na atoms and BN sheet on different adsorption sites were calculated according to equation (1), the results were showed in Table 1. From the Table 1, we found that the binding energy of Na on different adsorption site were more than the cohesive energy of Na atom (1.113eV), it showed that the cluster phenomenon of Na atoms does not occur and Na atoms can adsorb the surface of BN sheet stably. The distance between Na atom and BN sheet was the shortest when Na atom adsorb on the top of N atom (T_N), at this time, the binding energy between Na atom and BN sheet was the largest. It showed that the structure of Na atom absorb at T_N site was the most stable. This result was similar to with the literature [16].

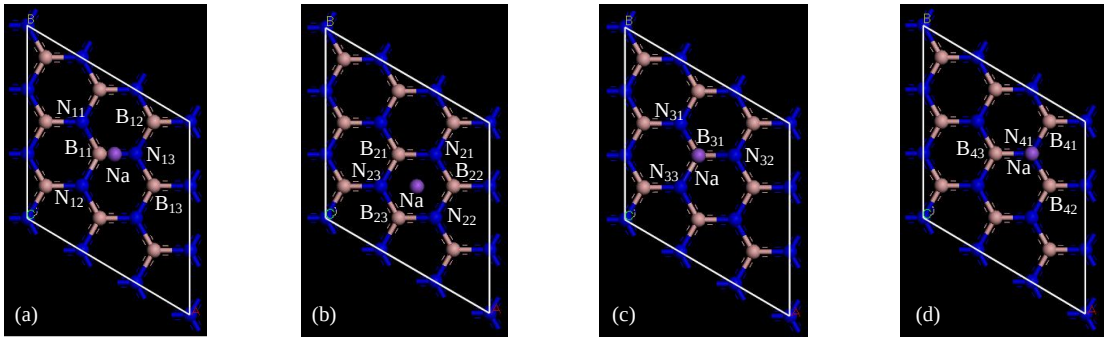


Figure 1. The adsorption structures of Na decorated BN sheet
(a)bridge site; (b)hollow site; (c)the top of B site; (d)the top of N site

Table 1. The adsorption energy and distance of Na-BN and Na-BN+H_2

	B	H	T_B	T_N
E_b/eV	1.807	2.129	1.870	2.371
$d_{Na\text{-}BN}$/nm	0.231	0.201	0.218	0.198
d_{av}/nm	0.143	0.142	0.144	0.142
E_{ab}/eV	0.276	0.290	0.277	0.269
$d_{H2\text{-}BN}$/nm	0.272	0.265	0.270	0.281

The density of states (DOS) distribution of Na atoms at the different adsorption site was shown in Figure 2. For the structure of Na atom adsorbed on B site, the seriously overlap between the Na atom and BN sheet were in the same energy range from -0.450~0.471eV, 0.793~1.426eV and 2.394~3.292eV (Figure 2a). For the structure of Na atom adsorbed on H site, the seriously overlap between the Na atom and BN sheet were in the same energy range from 1.990~3.223eV (Figure 2b). For the structure of Na atom adsorbed on T_B site, the seriously overlap between the Na atom and BN sheet were in the same energy range from -0.469~0.441eV, 0.487~1.397eV and 2.710~3.298eV (Figure 2c). For the structure of Na atom adsorbed on T_N site, the seriously overlap between the Na atom and BN sheet were in the same energy range from 1.868~4.230eV (Figure 2d). It was be found that Na atom T_N site adsorption structure has the largest overlap range between Na atoms and BN sheet. Natural bond orbit (NBO) analysis was used to study the binding energy of the four structures further. It has indicated that the bond of B site's Na atom and the nearest neighbor B, N atoms displays hybridization $s^{0.28}p^{0.69}d^{0.03}$, the bond of H site's Na atom and the nearest neighbor B, N atoms displays hybridization $s^{0.26}p^{0.71}d^{0.03}$, the bond of TB site's Na atom and the nearest neighbor B, N atoms displays hybridization $s^{0.27}p^{0.71}d^{0.02}$, the bond of TN site's Na atom and the nearest neighbor B, N atoms displays hybridization $s^{0.98}p^{0.02}$. It showed that the hybridization of above four structures are basically the same, but the hybridization of Na atom on T_N site adsorption concentrated in s orbit, this further explains the reason for the stronger binding energy of Na atom on T_N site adsorption.

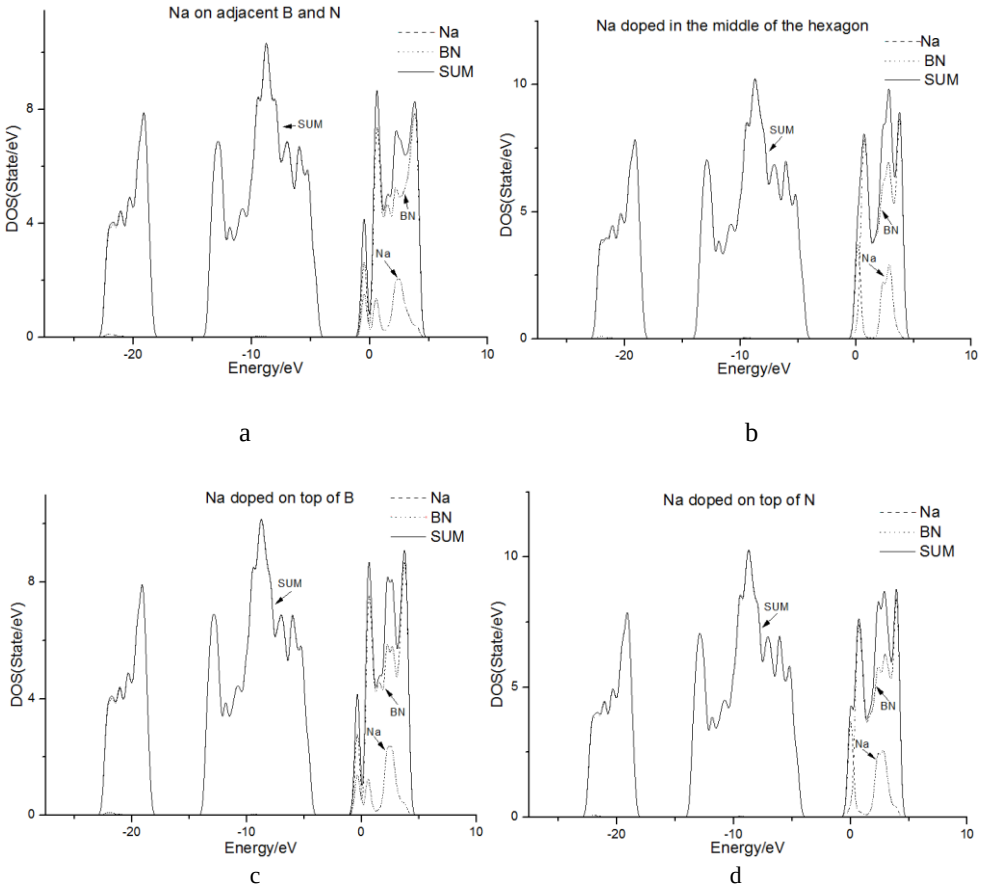


Figure 2. DOS of the different structure of Na adsorption site

3.2. Adsorption of H2 Molecules on Pure BN Sheet

According to the symmetry, there were four possible adsorption sites for the adsorption of pure BN sheet by H_2 molecules (T_B, T_N, B and H site). Average adsorption energy of H_2 molecules with different adsorption sites have been calculated according to the Equation 2 and listed in Table 2. The structures of H_2 molecules changed little after geometric optimization. The adsorption energy of H_2 molecule at H site was the strongest, it showed that H_2 molecules are more easily adsorbed to the H site. The results also showed that the adsorption energy of H_2 molecules adsorbing pure BN sheet was low (~0.27 eV). For this reason, metal Na decorated BN sheet have been designed to increase hydrogen storage rate.

3.3. The Adsorption Energy, Geometric Structure and Electronic Structure of H2 Molecules Adsorbing Na Decorated BN Sheet

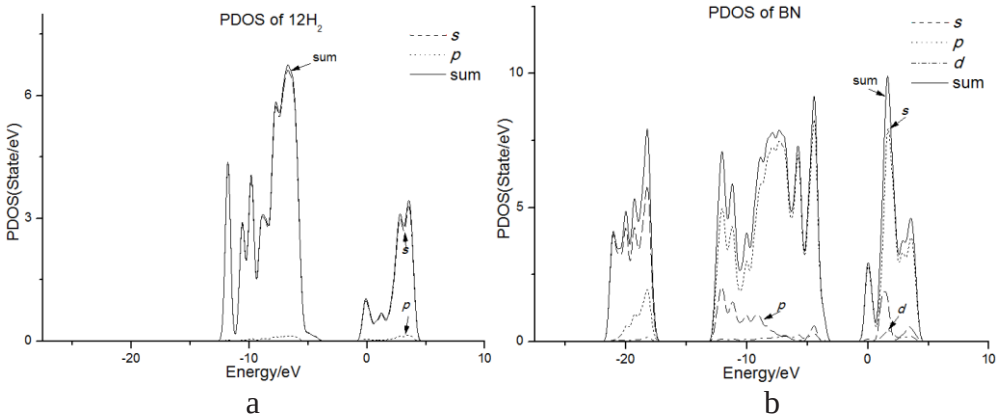
Studies have shown that metal atom can improve the hydrogen storage performance of nanomaterials greatly. Since the structure of TN site's Na atom decorated BN sheet was the most stable, the H_2 molecules were placed around the Na atom. When the number of H_2 molecules exceeds fourteen, most of the H_2 bonds were broke and form hydrogen atoms, and the adsorption energy tends to rise. Therefore, the geometric structure, electronic structure and hydrogen storage rate of 1~12 H_2 molecules adsorbed around decorated TN site's Na atom have been discussed respectively. Structural parameters and adsorption energy were listed in Table 2. As the number of adsorbed H_2 molecules increases: (1) The bond length of H_2 molecular did not change much (maximum increase of 1.9%), so all of the H_2 atoms exist as hydrogen molecules; (2) The distance between the Na atom and the BN sheet tended to decrease, and the distance between the H_2 molecule and the BN sheet tended to increase. When six H_2 molecules were adsorbed, the distance between Na atom and BN sheet

increases, the distance between H_2 molecules and BN sheet decreases, and the average adsorption energy of H_2 molecules increases. The reason for this phenomenon was that the six H_2 molecules adsorbed around the TN site's Na atom were just above the six adjacent BN sheet hollow. According to the calculation results in Table 1, the H_2 molecule has the largest adsorption energy and the smallest adsorption distance. This may be the reason why the adsorption energy increases when six hydrogen molecules were adsorbed. (3) According to the calculated results of standard deviation of distance between H_2 molecules and BN sheet, we can find that the standard deviation increase as the number of H_2 molecules increase. It was indicated that H_2 molecules would not be distributed on one plane and tend to be messy. (4) The adsorption energy of H_2 molecule was between ~0.83 - ~0.49eV/H_2 and the distance between H_2 molecule and Na-BN sheet was between ~0.33 - ~0.26nm, this showed that chemical adsorption between H_2 molecules and Na-BN sheet. With the increase of the number of H_2 molecules, the adsorption energy of H_2 molecules decreases gradually, but the adsorption energy tends to increase when the number of adsorbed molecules exceeds eight. In order to achieve rapid hydrogen absorption and desorption at room temperature, the number of H_2 molecules can be adsorbed was twelve at most. The average adsorption energy was 0.530 eV/H_2, and the corresponding hydrogen storage rate was 8.9433 wt%.

Table 2. The adsorption energy and structure parameter of Na-BN+nH_2(n=1~12)

	1H_2	**2H_2**	**4H_2**	**6H_2**	**8H_2**	**10H_2**	**12H_2**	**14H_2**	**16H_2**
E_{ab}(eV/H_2)	0.826	0.595	0.501	0.521	0.483	0.515	0.530	0.553	0.555
d_{H2}(nm)	0.754	0.757	0.764	0.753	0.760	0.759	0.757	-	-
$d_{Na\text{-}BN}$(nm)	0.359	0.357	0.356	0.401	0.325	0.332	0.322	-	-
$d_{H2\text{-}BN}$(nm)	0.269	0.274	0.272	0.264	0.298	0.318	0.329	-	-
$SE_{H2\text{-}BN}$	-	0.000	0.003	0.002	0.066	0.083	0.066	-	-
W(wt%)	0.812	1.610	3.170	4.681	6.145	7.565	8.943	-	-

To further analyze the interaction between H_2 molecules and Na-BN sheet, reveal the key factors affecting structural stability, the partial density of states (PDOS) for adsorption of twelve H_2 molecules compound has been calculated (Figure 3). The PDOS of Na-BN+12H_2 below the Fermi level was mainly contributed by the BN sheet and the H_2 molecules, and above the Fermi level were contributed by the BN sheet, H_2 molecules and Na atom. Due to the hybridization between H_2 molecules and Na-BN sheet, a few electrons of H_2 molecule were in p orbital to form $s^{0.98}p^{0.02}$ hybrid, resulting in a slight increase in the bond length of the adsorbed H_2 molecules than the free H_2 molecule bond length.



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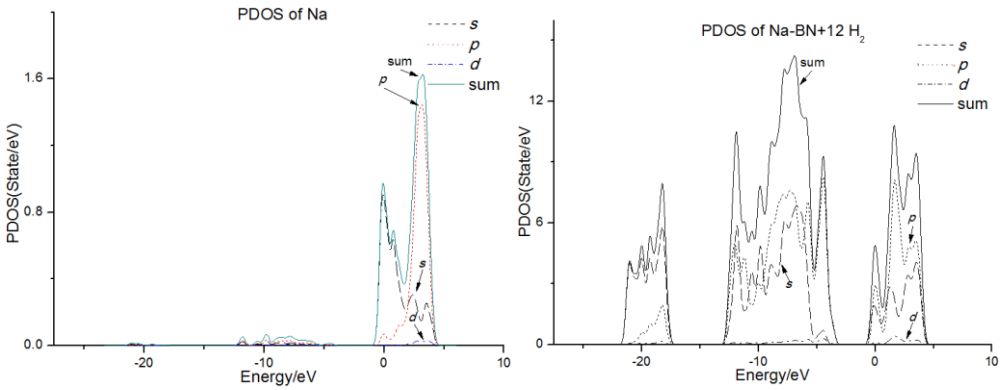

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Figure 3. PDOS of Na-BN+12H_2

3.4. Mulliken Population Analysis

In order to study the charge distribution of Na-BN, the Mulliken population has been calculated. The results were showed in Table III. Since the electronegativity of N, B and Na decreases in turn (3.04>2.04>0.93), the Na and B atoms in the system were positive charge and the N atoms were negative charge.

Table 3. Mulliken charge population of Na-BN

B site	**$N_{1,1}$**	**$N_{1,2}$**	**$N_{1,3}$**	**$B_{1,1}$**	**$B_{1,2}$**	**$B_{1,3}$**	**Na**
	-0.354	-0.355	-0.337	0.142	0.316	0.320	0.028
T site	$N_{2,1}$	$N_{2,2}$	$N_{2,3}$	$B_{2,1}$	$B_{2,2}$	$B_{2,3}$	Na
	-0.342	-0.345	-0.340	0.309	0.322	0.316	0.152
T_B site	$N_{3,1}$	$N_{3,2}$	$N_{3,3}$		$B_{3,1}$		Na
	-0.354	-0.358	-0.354		0.141		0.025
T_N site		$N_{4,1}$		$B_{4,1}$	$B_{4,2}$	$B_{4,3}$	Na
		-0.336		0.299	0.294	0.302	0.182

By comparing the Mulliken population of Na-BN+12H_2 (Table 4), it was found that the charge of B and N atoms did not change much (<11%), and the charge of Na atom increased by 55.5%. Polarization occurs in the charge distribution of H_2 molecules, which was why the ability of Na-BN adsorbing H_2 molecules was enhanced. Literature [18-24] studied the effect of external electric field on the hydrogen storage performance of graphene modified by Li atom and reached similar conclusions [25-30].

4. Conclusıons

With the calculation of hydrogen storage performance of Na decorated BN sheet by the first principle, it was found that: (1) The Na atom has the highest binding energy for the adsorption of BN sheet on the TN position, and the structure is the most stable. (2) The H_2 molecules have the highest adsorption energy for the pure BN sheet on the H site. (3) Na decorated BN sheet can increase the adsorption energy of H_2 molecules significantly. As the number of adsorbed H_2 molecules increases, the average adsorption energy decreases. However, when the number of H_2 molecules exceeds eight, the average adsorption energy increases. When the number of H_2 molecules exceeds twelve, the hydrogen bonds break and form H atoms. (4) In order to achieve rapid hydrogen absorption and desorption at room temperature, Na-BN sheet can adsorb up to 12 H_2 molecules. The average

adsorption energy is 0.530eV/H_2, and the hydrogen storage rate can reach 8.943wt%.

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