Stable Two Dimensional Na Decorated BeN4: A Potential Candidate for Hydrogen Storage

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Abstract

Hydrogen, being a powerful energy carrier, possesses the ability to transform the present carbon economy to green hydrogen economy. Since wide range of resources are available for its production, reversible hydrogen storage is the prevalent challenge. Surface activation by adsorption has been reported to increase the hydrogen uptake, thus boosting the storage capacity. In this work, Sodium (Na) decorated Beryllonitrene (BeN₄) monolayer has been identified as a hydrogen storage material using first-principles calculations. Our results reveal that Na decorated BeN₄ has ability to adsorb up to 12 H₂ molecules, leading to high gravimetric density of 4.26 wt%. The adsorption energy per H₂ (adsorbate) is moderate i.e., between 0.13 and 0.298 eV, good enough for hydrogen storage in practical applications. AIMD simulations disclose that adsorbate experiences no kinetic hinderance in desorption. Moreover, the desorption temperature of H₂ molecule on NaBeN₄ monolayer (substrate) varies from 162.5 to 382 K, confirming the reversibility of substrate and thus ensuring its potential for hydrogen storage medium. The short recovery time predicts that the substrate responds rapidly in presence of H₂ molecules, which guarantees the fast kinetics of adsorbate. Our calculations predict Na-decorated BeN₄ monolayer as an excellent candidate for reversible and high-capacity hydrogen storage material.

Introduction

Recent advancements in scientific research have predicted hydrogen to be a promising source of energy for future needs, minimizing world’s dependence on fossil fuels.¹ Upcoming years will see an energy transition from finite carbon economy to green hydrogen economy. The hydrogen economy, first conceptualized in 1970, comprises of a network of production, storage, transportation and refueling of hydrogen powered systems. Hydrogen can be generated from clean technologies as electrolysis from renewable energy resources (hydel and wind energy), nuclear heat and reformation of fossil fuels. It is indeed a sustainable and environment friendly source of energy.²⁻⁵ However, to implement it as an energy resource, hydrogen storage is a prevailing challenge. In the past few years, several techniques have been tested to meet the requirements of materials for hydrogen storage such as hydrogen liquefaction, physical adsorption, high pressure gas storage, and chemical absorption.⁶⁻¹⁵ The major challenges for materials include large volumetric and gravimetric density, reversibility, mild operational temperature and pressure, fast kinetics, high storage performance, moderate heat of formation, high security, long life cycle, and cost-effectiveness.¹⁶⁻¹⁸

The two-dimensional materials possess unique properties such as, high surface to volume ratio and great strength which permits adsorption of hydrogen molecules.¹⁹ Furthermore, they have high flexibility and ultra-low weight which makes them suitable candidates for hydrogen storage and transportation.²⁰⁻²⁴ Hydrogen adsorption on 2D materials is an advantageous technique as the materials used for adsorption are porous and fulfill most of the mentioned requirements. Due to the presence of weak van der Waals forces, no permeation of hydrogen into substrate takes place, hence resisting structural and electronic modifications. Moreover, uptake and release of hydrogen is rapid ensuring the reversibility of substrate.
Adsorption energy is moderate due to absence of any strong bonds. High temperatures are desirable for desorption of \( \text{H}_2 \) from substrate for the fast kinetics and reversibility of hydrogen adsorption-desorption due to weak interactions. Pristine monolayers have small substrate-adsorbate binding energies to adsorb hydrogen molecules. Light-weight alkali metals like Li, Na and K decorated on 2D materials have been reported to favor the adsorption with large binding energies, and thus enhance the hydrogen storage capacity and fasten the rate of adsorption. Additionally, alkaline earth metals and transition-metal dichalcogenides (TMDs) have been reported to modulate the hydrogen storage properties of 2D materials.\(^7,13,25–28\)

Bafekry et al.\(^29\) carried out first-principles calculations on monolayer and few-layer BeN\(_4\) to study its structural, electronic, dynamical, and optical properties. Monolayer and bilayer revealed a semi-metallic character while other structures had a metallic character. The electronic and optical properties assured it as a suitable material for optoelectronic devices. Cheng et al.\(^30\) performed DFT calculations to examine feasibility of 2D BeN\(_4\) as an anode material for metal-ion batteries. The study was carried out by adsorption of alkali metal Li/Na/K on porous BeN\(_4\). The results suggested that Dirac cone in BeN\(_4\) can only adsorb K thus it can form an ideal anode material for Potassium ion batteries.

Wang et al.\(^31\) reported the hydrogen storage performance of Li, Na an K decorated Borophene. The results revealed that structures were stable even at 300 K. The achieved gravimetric density was 13.96 wt% which ensures the substrate to be an ideal candidate for hydrogen storage. Recently, the successful synthesis of a novel 2D material BeN\(_4\) (Beryllonitrene) has been reported by Bykov et al.\(^32\) The calculations revealed its graphene-like structural and electronic properties with slightly distorted honeycomb structure and Dirac points at fermi energy level. Since its synthesis, several studies\(^29,30,33–38\) have already been conducted on BeN4 to gain further insights. Since metal decoration on 2D materials enhances the hydrogen storage capacity, Sodium (Na) decoration of BeN4 has been studied here to investigate the modulation of hydrogen storage capacity of BeN4. Na decoration indicates the deposition of Na atoms onto the surface of the BeN4 material. This process increases the number of active sites on the surface of the material, ultimately improving the amount of hydrogen that can be stored. Our results can pave the way towards the development of novel materials with improved hydrogen storage capacities.

**Computational Methods**

Density functional theory (DFT)\(^{39,40}\) calculations were performed using Vienna ab initio package (VASP).\(^{41,42}\) Projected augmented wave (PAW)\(^{43}\) method was adopted to incorporate the interactions between valence and core electrons. The generalized gradient approximation (GGA) with Perdew-Burke Ernzerhof (PBE)\(^{44}\) was used for plane-wave expansion. Plane wave cut-off energy was set to 500 eV. For Brillouin zone sampling, a k-mesh of 5×5×1 and 7×7×1 was adopted for structural optimization and self-consistent field (scf) calculations, respectively, using Monkhorst Pack approach.\(^{45}\) A vacuum of 20 Å was added along z-axis to avoid interaction between adjacent layers. The energy convergence criteria in self
consistent field were adjusted to $10^{-5}$ eV. The structures were allowed to relax until Hellman Feynman forces reached 0.01 eVÅ$^{-1}$. A supercell of $3\times3\times1$ was considered to study the geometry of structures. The ab-initio molecular dynamics (AIMD)\textsuperscript{46} were used to monitor the finite-temperature dynamic pathways at 300 K for 2.5 ps. After relaxation, upto 12 hydrogen molecules were inserted in the supercell of substrate to examine the hydrogen adsorption. The van der Waals correction was incorporated using Grimme's DFT-D3 approach.\textsuperscript{47}

The adsorption energy per $\text{H}_2$ ($E_{\text{ads}}$) of Na-decorated $\text{BeN}_4$ is calculated as

$$E_{\text{ads}} = \frac{E_{\text{NaBeN}_4} + nE_{\text{H}_2} - E_{n\text{H}_2+\text{NaBeN}_4}}{n}$$

Here $E_{\text{NaBeN}_4}$ is the energy of Na decorated $\text{BeN}_4$, $E_{n\text{H}_2+\text{NaBeN}_4}$ is the total energy of $n$ number of hydrogen molecules adsorbed on $\text{BeN}_4+\text{Na}$ system and $nE_{\text{H}_2}$ is the energy of hydrogen molecule.

The gravimetric density (wt\%) is calculated using following equation:

$$\text{wt\%} = \frac{nW_{\text{H}_2}}{nW_{\text{H}_2} + W_{\text{NaBeN}_4}} \times 100$$

where $n$ is the number of $\text{H}_2$ molecules, $W_{\text{H}_2}$ is the molecular weight of a single $\text{H}_2$ molecule, and $W_{\text{NaBeN}_4}$ is the weight of the Na decorated $\text{BeN}_4$ monolayer.

**Results And Discussion**

The optimized $\text{BeN}_4$ has P1(1) space group with lattice parameters of $a = 12.81$ Å, $b = 10.98$ Å. The $\text{BeN}_4$ monolayer comprises of Be supported polymeric nitrogen chains. As predicted in Fig. 1 (a), the monolayer is a network of pentagons ($\text{BeN}_4$) and hexagons ($\text{Be}_2\text{N}_6$). It possesses a graphene-like slightly distorted structure with a Dirac cone about fermi level indicating its semi-metallic character as presented in Fig. 1 (c). Dirac cones exhibit a linear energy-momentum dispersion relation near fermi level ensuring a high carrier mobility. Around fermi level, electron and hole states are symmetric over the energy range of 2 eV. The density of states reveals a high contribution from N atoms in both conduction and valence bands. Around 1 eV in conduction band, band structure reveals the presence of graphene-like van Hove singularity\textsuperscript{48} which develops the occupancy of huge number of electrons. In the nitrogen chains, average N-N bond length is 1.344 Å which is in an intermediate between the single N-N bond length (1.346 Å) and double N=N bond length (1.342 Å), in consistency with the previously reported values.\textsuperscript{32,36} Average Be-N bond length is 1.74 Å. Figure 1 (b) depicts the isosurface of charge density difference to incorporate the metal atom (Na) within the $\text{BeN}_4$ chains. The pink regions indicate a charge loss whereas the blue regions show the charge accumulation. Beryllium atoms in the chain gain electrons while Nitrogen atoms lose electrons, developing an internal electric field.
The porous character of BeN₄ allows deposition of metal atom (Na) on its surface, increasing the number of active sites and consequently enhancing the hydrogen adsorption properties of the BeN₄. Na decoration on the surface of BeN₄ is depicted in Fig. 2 (a). The average Na-N bond length is 2.811 Å. In addition, the presence of Na atoms on the surface of the material increases the stability of material against oxygen and moisture, making it highly resistant to performance degradation. After the adsorption of Na-atom on BeN₄, it is observed that the character of bandgap changes to metallic and the Dirac cone shifts downward toward valence band, as shown in Fig. 3 (a).

Charge density analysis shows that Na atom transfers −1.00 e charge to N atoms of BeN₄. On adsorption of one hydrogen molecule on substrate, 0.012 e charge shifts from adsorbate to substrate. Due to increase in active sites by Na decoration, H₂ molecules can be widely adsorbed around the metal atom (Na). The odd number of electrons in the system and high electron densities near fermi energy level shows the metallic character of BeN₄. We have investigated hydrogen adsorption mechanism of the BeN₄ structure to verify its applications in H₂ based energy storage devices. Hydrogen atoms were added near Na atom and the system was allowed to relax. The first hydrogen molecule was added at about 2 Å from the Na atom and optimized. On each step of hydrogen adsorption, geometry optimization and adsorption energy were calculated. The adsorption energies were calculated with GGA and with the incorporation of long-range van der Waals (vdW) forces, increasing the energies. Decrease in adsorption energy is noticed with increase of hydrogen molecules through GGA, whereas it is random with the inclusion of vdW correction. The optimized structure of NaBeN₄ with adsorbed hydrogen molecules is shown in the Fig. 2 (b-f) and the calculated adsorption energies are presented in Table 1.

To determine the maximum hydrogen storage capacity of the substrate, multiple hydrogen molecules were adsorbed and tested. The Fig. 2 suggests that Na decorated BeN₄ has capacity to adsorb upto 12 H₂ molecules, leading to gravimetric density of 4.26 wt%. The stable configuration of the Na-BeN₄ is expected to be the one with 12 adsorbed H₂ molecules with highest storage capacity of 4.26 wt%. The adsorption energy per H₂ varies between 0.126 and 0.298 eV, as shown in Table 1, which is reasonable for practical applications. Gradually increasing the number of adsorbate molecules from 1 to 12 enhances the gravimetric density from 0.369–4.262%, respectively. It is clear from adsorption energies that Na is strongly bound to the BeN₄, and hydrogen molecules are adsorbed to substrate with less binding energy which is suitable for fuel applications.
Table 1

<table>
<thead>
<tr>
<th>nH₂</th>
<th>E_ads (eV)</th>
<th>H-H (Å)</th>
<th>wt%</th>
<th>T_D (K)</th>
<th>Recovery time τ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.126</td>
<td>0.759</td>
<td>0.369</td>
<td>162.5</td>
<td>1.35×10⁻¹⁰</td>
</tr>
<tr>
<td>3</td>
<td>-0.265</td>
<td>0.751</td>
<td>1.100</td>
<td>339.7</td>
<td>2.85×10⁻⁰⁸</td>
</tr>
<tr>
<td>6</td>
<td>-0.298</td>
<td>0.751</td>
<td>2.177</td>
<td>381.9</td>
<td>1.02×10⁻⁰⁷</td>
</tr>
<tr>
<td>9</td>
<td>-0.291</td>
<td>0.752</td>
<td>3.231</td>
<td>372.9</td>
<td>7.79×10⁻⁰⁸</td>
</tr>
<tr>
<td>12</td>
<td>-0.283</td>
<td>0.753</td>
<td>4.262</td>
<td>363.0</td>
<td>5.77×10⁻⁰⁸</td>
</tr>
</tbody>
</table>

The desorption temperature (T_D) of the Na decorated BeN₄ for the adsorbed hydrogen molecules is calculated by van't Hoff equation given by

$$ T_D = \frac{E_{ads}}{k_B} \left( \frac{\Delta S}{R} - \ln p \right)^{-1} $$

where E_ads is adsorption energy per H₂ molecule, k_B is Boltzmann constant (1.389×10⁻²³ JK⁻¹), ΔS is the entropy change in H₂ from gas to liquid phase (75.44 Jmol⁻¹K⁻¹), R is the universal gas constant (8.314 Jmol⁻¹K⁻¹), and p is the equilibrium pressure (1 atm). The average desorption temperature of H₂ molecule for Na-decorated BeN₄ is 324 K, confirming the evaporation of adsorbate from substrate.

Recovery time (τ) is an important factor to illustrate the rate of adsorbate's desorption from the substrate. Desorption and adsorption energies are equal since the adsorbate and substrate interact with each other, then recovery time can be determined as follows:

$$ \tau = \omega^{-1} \exp \left(-\frac{E_{ads}}{k_BT}\right) $$

here ω, T, k_B, and E_ads are the attempt frequency, temperature, Boltzmann constant, and adsorption energy, respectively. The short recovery time suggests that the substrate responds quickly in presence of H₂ molecules, assuring the fast kinetics of adsorbate.

Table 1 shows that variation in number of molecules of adsorbate, modulates the recovery time. Thus, substrate is expected to respond more rapidly and effectively to adsorbate (H₂ molecules).
To study system stability at room temperature, molecular dynamic simulation is needed. We performed AIMD in a microcanonical (NVE) ensemble with Nose-Hoover thermostat. The simulations predict that system experiences no kinetic hinderance in desorption, i.e., the \( \text{H}_2 \) uptake and release is rapid. The system was heated from 0 to 300 K for 7 ps with 1 fs time step and the results of ab initio molecular dynamics (AIMD) simulations are presented in Fig. 3 (g).

PDOS analysis was done to investigate orbital interaction before and after Na atom decoration to BeN\(_4\) structure. PDOS for Na 2s state for isolated Na atom and after decoration to the BeN\(_4\) system is plotted as shown in Fig. 1 (c). After decoration of Na atom, a reduction in Na-2s state is observed, in Fig. 3 (b-f), as compared to the independent Na-2s state. Upon Na atom adsorption, enhancement in N-2p state near Fermi level is observed. This indicates transfer of charge from Na-2s state to N-2p state. This transfer of charge is responsible for Na bonding on BeN\(_4\) structure. Change in TDOS is due to interaction of N-2p and Na-2s states. shows that there is a drop in Na-2s states after hydrogen adsorption which indicates that adsorption on the system is not purely physisorption but also some charge transfer occurs which provides suitable adsorption energy for hydrogen.

**Conclusions**

DFT calculations have been performed on recently synthesized two-dimensional BeN4, decorated with Na, to examine its geometrical, electronic and hydrogen storage properties. Our results suggest that Na-decoration transforms the band structure to metallic and shifts the Dirac cone to valence band. Moreover, it adsorbs maximum of 12 hydrogen molecules with a storage capacity of 4.26%. The average adsorption energy per \( \text{H}_2 \) was \(-0.253\) eV which is good for hydrogen storage applications. Moreover, the average desorption temperature of \( \text{H}_2 \) molecule on NaBeN4 was found to be 324 K, confirming the reversibility of substrate. AIMD calculations reveal the structure's thermodynamic stability and thus assure of no kinetic resistance in desorption. Short recovery time indicates fast response of substrate to adsorbate. In sum, our calculations predict Na-decorated BeN\(_4\) monolayer as a potential candidate for reversible and high-capacity new-generation hydrogen storage material.

**Declarations**

**Author Contributions**

We strongly encourage authors to include author contributions and recommend using CRediT for standardised contribution descriptions. Please refer to our general author guidelines for more information about authorship.

**Conflicts of interest**

There are no conflicts to declare.
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References


Figures
Figure 1

(a) The rectangular structure, (b) isosurface of differential charge density and (c) projected band structure and density of states of BeN4

Figure 2

(a) Na decorated BeN4 (b-f) adsorption of H₂ molecules on Na-decorated BeN₄
Figure 3

The projected band structure and density of states for (a) Na decorated BeN₄, (b-f) Na decorated BeN₄ with 1, 3, 6, 9, and 12 adsorbed hydrogen molecules, respectively, and (g) ab initio molecular dynamics (AIMD)