Enhancement in hydrogen storage capacities of light metal functionalized Boron–Graphdiyne nanosheets

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Abstract
The recent experimental synthesis of the two-dimensional (2D) boron-graphdiyne (BGDY) nanosheet has motivated us to investigate its structural, electronic, and energy storage properties. BGDY is a particularly attractive candidate for this purpose due to uniformly distributed pores which can bind the light-metal atoms. Our DFT calculations reveal that BGDY can accommodate multiple light-metal dopants (Li, Na, K, Ca) with significantly high binding energies. The stabilities of metal functionalized BGDY monolayers have been confirmed through ab initio molecular dynamics simulations. Furthermore, significant charge-transfer between the dopants and BGDY sheet renders the metal with a substantial positive charge, which is a prerequisite for adsorbing hydrogen (H2) molecules with appropriate binding energies. This results in exceptionally high H2 storage capacities of 14.29, 11.11, 9.10 and 8.99 wt% for the Li, Na, K and Ca dopants, respectively. These H2 storage capacities are much higher than many 2D materials such as graphene, graphane, graphdiyne, graphyne, C2N, silicene, and phosphorene. Average H2 adsorption energies for all the studied systems fall within an ideal window of 0.17–0.40 eV/H2. We have also performed thermodynamic analysis to study the adsorption/desorption behavior of H2, which confirms that desorption of the H2 molecules occurs at practical conditions of pressure and temperature.

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1. Introduction
Due to the continuous increase in global energy utilization and the effects of fossil fuel consumption on the climate, the development of sustainable and renewable energy supplies is a matter of urgency. Hydrogen (H2) is considered an ideal alternative to the depleting fossil fuels due to attractive properties such as high energy density with no harmful effects on the environment. However, an efficient way of storing H2 is the main obstacle towards its realization as a green and clean energy carrier [1–4]. Among different storage routes, 2D material-based H2 storage seems to be the most sustainable option provided a suitable material is available, which meets the criteria proposed by US Department of Energy.

Carbon nanostructures (CNs) is a family of materials, which has been studied extensively for H2 storage applications in different morphologies, such as carbon nanotubes, graphene, graphane, graphdiyne, graphyne and many others [5–14]. However, the limitation of CNs, in their pristine form, is the weak binding with H2 molecules, which restricts their applications as efficient H2 storage materials due to small H2 uptake or low operating temperatures [15]. Thus, the binding energies of H2 with the host CNs must be enhanced for storage at ambient conditions. Several techniques have been employed for improving H2-CNs binding, e.g., spillover effect, defects formation in host materials, application of electric fields, inducing charges, and metal functionalization [16–20].

Functionalization of CNs and other nanostructures by introducing various elements for H2 storage has been comprehensively studied. Zhou and Szpunar investigated H2 storage properties of graphene sheets doped with Pd nanoclusters. They found that Pd clusters of 5–45 nm uniformly distributed over the graphene nanosheet attain H2 storage capacity of 6.7 and 8.7 wt% at pressures of 50 and 60 bar, respectively [21]. Zhou et al. synthesized Ni/graphene composites in which Ni clusters of 10 nm are uniformly dispersed over the graphene surface and studied their H2 storage...
capacities. At ambient conditions an H₂ storage capacity of 0.1 wt% was achieved, and it could be increased to 1.2 wt% at a pressure of 60 bar [22].

Theoretical studies of metal functionalized CNs other than graphene for H₂ storage have also been carried out. Liu et al. used first principles calculations based on density functional theory (DFT) to study the structural, and H₂ storage properties of Mg doped γ-graphyne sheets and obtained a storage capacity of 10.6 wt% [23]. It was reported that the application of electric field would restrict the aggression of Mg dopants and the adsorbed H₂ molecules bind with binding energy range of 0.28 eV/H₂, which falls within the desired window. Pan et al. used DFT calculations to study the H₂ storage properties of various CNs such as C₄₀, C₄₁, C₆₃, C₆₄ and C₆₅ doped with Ca at various concentrations. They concluded that Ca binds strongly with the CNs and anchor multiple H₂ molecules attaining a high H₂ storage capacity of up to 8.6 wt% [24]. Another DFT study by Mohajeri and Shahsavari investigated metal functionalization of a graphyne monolayer under nitrogen and sulphur co-doping. They reported high H₂ storage capacities of 9.0 and 9.3 wt% for Li and Na metal doping, respectively [25].

The above studies demonstrate that metal functionalization of CNs can play a vital role in improving H₂ binding with the host material. A very recent addition to the family of two-dimensional CNs is the boron-graphyne (BGDY) nanosheet, which has been synthesized via a bottom-up synesthetic approach [26]. Among several attractive properties of BGDY such as enhanced optical, thermal stability, mechanical stability, and thermal conductivity, the presence of boron centres uniformly distributed in a carbon network creates additional binding cites for metal centres. Mortazavi et al. studied the structural, electronic, thermal, mechanical, optical and metal storage properties of BGDY by means of DFT coupled with molecular dynamics simulations [27]. Under the application of mechanical strain, it was concluded that this porous 2D monolayer preserves superstretchability. The authors further studied the application of BGDY as high capacity anode material for Li, Na and Ca ion batteries. Motivated by the enhanced metal storage properties of BGDY, we have employed spin-polarized periodic boundary condition DFT calculations using the VASP code [28,29]. In these calculations, the generalized gradient approximation (GGA) PBE exchange-correlation functional has been used [30]. We have employed projector-augmented wave (PAW) method to deal with the ion–electron interactions [31]. Empirical van der Waals corrections have been included using the D3 dispersion correction of Grimme et al. [32] The Brillouin zone (BZ) has been sampled by Monkhorst–Pack scheme with a mesh size of 3 × 3 × 1 for geometry optimization and 7 × 7 × 1 for obtaining density of states [33]. A vacuum space of 20 Å has been inserted, which is large enough to evade the possible interactions between periodic images along the z-axis. In the geometry optimizations, the convergence criteria for the total energies and forces have been set at 10⁻⁵ eV and 0.01 eV/Å, respectively. Binding of metal dopants to the BGDY monolayer involves charge transfer mechanism, which has been studied by means of Bader charge analysis [34]. Binding energies per dopant (Eₜ) of metal adatoms on BGDY are calculated using the following equation:

\[ Eₜ = \frac{E(BGDY + nX) - E(BGDY) - nE(X)}{n} \]  

where X = Li, Na, K, Mg, Ca, and n = 1–4. In this equation, the first, second and third terms represent the total energies of BGDY bonded with n metal dopants, pristine BGDY monolayer and metal dopants, respectively.

3. Results and discussion

The optimized structure of BGDY is shown in Fig. 1. The BGDY monolayer used in this study has 14 atoms (C₁₂B₂) consisting of two types of C–C bond lengths of 1.23 Å and 1.35 Å, and a B–C bond length of 1.51 Å. The calculated lattice constant of 11.85 Å and the bond lengths mentioned above agree well with the previous study that used the more reliable hybrid GGA functional HSE06 [27]. In pristine form, BGDY preserves a semiconducting behavior with a energy gap (Eₚ) of 0.485 eV, as evident from a total and partial density of states plots (Fig. 1(c)). However, this Eₚ value is underestimated due to the well-known inability of the PBE functional to calculate the exact Eₚ. A more accurate Eₚ value has been calculated by Bohay et al. using the HSE06 functional they obtained a value of 1.15 eV [27]. As the mechanical, thermal and dynamic stability of the BGDY monolayer has already been studied in Reference [27], we start by investigating its metal doping capacities.

Like most of the CNs, pristine BGDY barely binds H₂, thus metal dopants (e.g., Li, Na, K, Mg, Ca) have to be introduced to enhance the BGDY-H₂ binding energies. The binding energies of these dopants over the BGDY monolayer should exceed their corresponding cohesive energies (Eₙ) to ensure a reversible doping mechanism. On the other hand, when Eₚ exceeds Eₚ, clustering of metal dopants would be a more likely outcome rather than binding to BGDY. The selection of alkali and alkaline metal dopants has been based on the
fact that these light elements, having lower cohesive energies, would make uniform scattering over the BGDY monolayer. We have considered all the possible binding sites on BGDY monolayer for metal doping and compare the $E_b$ values. The lowest $E_b$ configurations yield $E_b$ values of $-2.95$, $-2.51$, $-2.91$, $-1.13$ and $-3.04$ eV for Li, Na, K, Mg and Ca, respectively. With the exception of Mg ($-1.51$ eV), these $E_b$ values are much higher than the corresponding cohesive energies of Li ($-1.63$ eV), Na ($-1.11$ eV), K ($-0.93$ eV) and Ca ($-1.84$ eV) [35,36]. Moreover, our calculated $E_b$ values for the studied dopants are higher than those of graphenylene, phosphorene, stanene, siligraphene (SiC$_7$) and graphdiyne nanosheets [5,20,37–39]. This indicates the potential of BGDY as a promising metal anchoring material.

Large surface to volume ratio due to its 2D nature and big pore size enables BGDY to accommodate more metal dopants. This would assist in achieving more active sites for the incoming H$_2$ molecules to be adsorbed on BGDY monolayers, which would result into a large H$_2$ gravimetric density. However, the introduction of metal dopants on BGDY will be associated with the transfer of charge from the former to the later. Thus, electrostatic repulsion between the cationic dopants could be a concern in achieving high metal doping concentration and consequently high H$_2$ storage capacity. Maintaining a reasonably high distance between the two adjacent metal dopants can solve this problem. For further metal adsorption, the BGDY doped with single metal dopant has been considered as initial structure. The second dopant is introduced on adsorption, the BGDY doped with single metal dopant has been considered all possible binding sites available on BGDY monolayer preserving a considerable large distance from the existing metal atom. The lowest energy structures among the considered configurations are associated with $E_b$ values of $-2.62$, $-2.10$, $-2.45$ and $-2.61$ eV, for Li, Na, K and Ca, respectively. Upon the introduction of second dopant, the reduction in $E_b$ values are 11.19, 16.33, 15.80 and 14.14% for Li, Na, K and Ca, respectively. Despite the decrease in $E_b$, we still obtain $E_b > E_c$, which indicates that the dopants dispersion over BGDY is preferred instead of metal clustering. We kept on adding more metal dopants as long as their $E_b$ is exceeding the $E_c$ values. The optimized structures of BGDY monolayers with maximum metal dopants considered in this study are shown in Fig. 2. For the third dopant, BGDY monolayer pre-adsorbed with two dopants and for the fourth dopant, BGDY pre-adsorbed with three dopants served as an initial structure. It is important to mention here that the minimum dopant-dopant distance at the highest doping concentrations for Li, Na, K and Ca has been found as 4.45, 5.16, 5.20 and 4.86 Å, respectively. Complete results for the structural parameters of all the systems at various doping concentrations are given in Table 1. The $E_b$ values in the case of four dopants for all the metals are still higher than their corresponding $E_c$ as shown in Fig. 3 (a).

In addition to the energetic stability, that is $E_b > E_c$, we have confirmed the thermal stabilities of BGDY monolayers loaded with four metal dopants of Li, Na, K and Ca by using ab initio molecular dynamics simulations (AIMD). This is done by employing Nose thermostat algorithm at 300 K for 6 ps with a time step of 1 fs. All the doped systems remained stable without significant structural deformation, which is evident from small variations in their energies (for further details see Fig. S1 of the Supplementary Information). This ensures the thermal stabilities of metal-doped BGDY monolayers.

As mentioned above, the metal-BGDY interactions involve charge transfer; we have employed Bader analysis to estimate the amount of charge transfer between the dopants to the BGDY monolayers. At a maximum doping concentration, that is BGDY-4X (X = Li, Na, K, Ca) each Li, Na, K and Ca dopants have transferred an average charge of 0.98, 0.68, 0.60 and 1.09 e to the monolayer, respectively. This implies that BGDY monolayers attain significantly

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**Table 1**

<table>
<thead>
<tr>
<th>System</th>
<th>$E_b$ per X (eV)</th>
<th>$E_b/E_c$</th>
<th>$D_1$ (Å) X-BGDY distance</th>
<th>$D_2$ (Å) X-X distance</th>
<th>Charge transferred Q (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BGDY-Li</td>
<td>$-2.95$</td>
<td>1.81</td>
<td>2.10</td>
<td>11.84</td>
<td>0.992</td>
</tr>
<tr>
<td>BGDY-2Li</td>
<td>$-2.62$</td>
<td>1.60</td>
<td>2.16</td>
<td>6.02</td>
<td>0.991</td>
</tr>
<tr>
<td>BGDY-3Li</td>
<td>$-2.32$</td>
<td>1.42</td>
<td>2.20</td>
<td>4.83</td>
<td>0.987</td>
</tr>
<tr>
<td>BGDY-4Li</td>
<td>$-2.13$</td>
<td>1.28</td>
<td>2.29</td>
<td>4.45</td>
<td>0.980</td>
</tr>
<tr>
<td>BGDY-Na</td>
<td>$-2.51$</td>
<td>2.61</td>
<td>2.39</td>
<td>11.84</td>
<td>0.992</td>
</tr>
<tr>
<td>BGDY-2Na</td>
<td>$-2.10$</td>
<td>1.89</td>
<td>2.43</td>
<td>5.93</td>
<td>0.991</td>
</tr>
<tr>
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<td>1.59</td>
<td>2.53</td>
<td>5.88</td>
<td>0.747</td>
</tr>
<tr>
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<td>1.44</td>
<td>2.58</td>
<td>5.16</td>
<td>0.680</td>
</tr>
<tr>
<td>BGDY-K</td>
<td>$-2.91$</td>
<td>3.13</td>
<td>2.73</td>
<td>11.84</td>
<td>0.914</td>
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<tr>
<td>BGDY-2K</td>
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<td>2.80</td>
<td>6.79</td>
<td>0.893</td>
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<tr>
<td>BGDY-3K</td>
<td>$-2.03$</td>
<td>2.18</td>
<td>2.81</td>
<td>5.81</td>
<td>0.727</td>
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<tr>
<td>BGDY-4K</td>
<td>$-1.78$</td>
<td>1.91</td>
<td>2.85</td>
<td>5.20</td>
<td>0.600</td>
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<tr>
<td>BGDY-Ca</td>
<td>$-3.04$</td>
<td>1.65</td>
<td>2.39</td>
<td>11.84</td>
<td>1.459</td>
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<tr>
<td>BGDY-2Ca</td>
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<td>2.46</td>
<td>8.71</td>
<td>1.139</td>
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<tr>
<td>BGDY-3Ca</td>
<td>$-2.44$</td>
<td>1.32</td>
<td>2.40</td>
<td>5.45</td>
<td>1.107</td>
</tr>
<tr>
<td>BGDY-4Ca</td>
<td>$-2.35$</td>
<td>1.27</td>
<td>2.48</td>
<td>4.86</td>
<td>1.070</td>
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</tbody>
</table>
high negative charges, leaving the dopants in cationic form with reasonably high partial positive charges. Bulk share of these donated charges has been captured by the C and B atoms of the BGDY monolayer, which are in close vicinity to the dopants. Depletion and accumulation of electronic charges has been calculated by the following relation and shown in Fig. 4.

\[
\Delta \rho = \rho(BGDY; X) - \rho(BGDY) - \rho(X)
\]  

Here the first, second and third terms represent the charge densities of doped BGDY, pristine BGDY, and the metal dopant, respectively.

Transfer of charges from the dopants would change the electronic properties of BGDY monolayers, which have been studied by density of states plots. Fig. 5 shows the partial density of states (PDOS) plot of BGDY doped with 4 Li atoms. One can see a transition from semiconducting to metallic BGDY upon the introduction of Li adatoms. The contribution appearing at the Fermi level \(E_F\) is from Li(s), which clearly overlaps with B(p) and C(p). This Li dopant is the one, which is bonded to BGDY monolayer in the vicinity of both B and C atoms. As indicated by in the Bader charge analysis that each Li dopant donates an average of 0.98 \(e\) to BGDY, thus the distinct peaks appearing between \(-3.70\) and \(-3.50\) eV on the left, and then \(0\) to \(2.0\) eV on the right side of \(E_F\) corresponds to Li(s) contributions to BGDY monolayer.

Similar to Li, the other dopants, Na, K and Ca, cause semiconducting to metallic transitions as shown in Figs. S2–S4 (supplementary information). For Na doping, the distinguishing peaks of Na(s) appear at \(-4.2\), \(-3.8\) and \(-0.92\) eV on the left and at \(0.20\), \(0.40\) and \(1.20\) eV on the right of \(E_F\). For K and Ca doping, the valence bands are mainly dominated by C(p) and B(p), with small contributions from the s orbitals of K and Ca. However, at the top of \(E_F\) the hybridization of K(s) and Ca(s) with those of C(p) and B(p) are more dominated as compared to the Li and Na cases, which is evident in Figs. S3 and S4, respectively.

So far we have discussed the structural, thermal stabilities, charge transfer and electronic properties, we will now move on to investigate the adsorption of \(H_2\) on metal-functionalized BGDY monolayers. Each system has four metal dopants, which are positively charged and capable of binding \(H_2\) molecules through electrostatic as well as van der Waals interactions. Each of the positively charged ions (Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Ca\(^{+}\)) generates a local electric field through which it polarizes the incoming \(H_2\) molecules and thus induces a local negative charge on \(H_2\). Induction of a charge on \(H_2\) results in a binding strength, which is much stronger than that of pristine BGDY-\(H_2\) binding and can be calculated by the following equation:

\[
E_b(H_2) = \{E(BGDY@4X:nH_2) - E(BGDY@4X) - n E(H_2)\} / n
\]  

In this equation, \(E_b(H_2)\) is the binding energies of \(H_2\) on metal
functionalized BGDY, and the first, second and third terms on the right-hand-side are the total energies of BGDY@4X bonded with n H2 molecules, pristine BGDY@4X and H2, respectively (where X = Li, Na, K and Ca and n = 1–4).

To avail all the active metal binding sites, we have introduced H2 molecules on each dopant of the functionalized BGDY monolayers in a stepwise mode. That is, in the first step four H2 molecules have been inserted on BGDY@4X and the systems are allowed to relax completely. Based on our previous experience, [12] a vertical adsorption of H2 to the metal dopant is more favorable. In the next step, we introduced a second H2 molecule on each dopant of the optimized BGDY@4X carrying 4 H2 molecules. For further H2 adsorption, a suitable distance of H2 with the metal dopants as well as among charged induced H2 molecules should be maintained to avoid the steric and electrostatic repulsion. Overall, each metal dopant X of BGDY@4X is bonded to two H2 molecules, thus a total of 8 H2 molecules have been adsorbed. This process is repeated until the systems reach saturation, that is the point where further H2 molecules would be repelled upon optimization.

It is important to mention here that the binding energies per H2 molecule (eq. (3)) is compared with the desired range of 0.15–0.60 eV/H2 each time an H2 is added to the system. We have concluded that each dopant can accommodate a maximum of 4 H2 molecules, which means that a total of 16 H2 could be adorned on BGDY@4X with H2 binding energies within the accepted range. The van der Waals corrected DFT Eb (H2) for all the systems with different H2 coverage are given in Fig. 3(b). One can clearly notice a decreasing trend in the Eb (H2) values upon the increasing H2 densities in Fig. 3(b). In case of BGDY@4Li, the binding energies vary from −0.297 to −0.170 eV per H2 from minimum to maximum H2 coverage. For the other dopants we obtain the following ranges of Eb (H2) per H2 from minimum to maximum H2 coverage: 0.343 to −0.186 (BGDY@4Na), −0.389 to −0.187 (BGDY@4K) and −0.408 to −0.206 (BGDY@4Ca) eV.

At a maximum H2 coverage the H2 storage capacities of 14.29, 11.11, 9.10 and 8.99 wt% have been achieved for BGDY@4Li, BGDY@4Na, BGDY@4K, BGDY@4Ca, respectively. These storage capacities are superior to those of other metal-doped monolayers such as graphene, h-BN, C2N, GDY, MoS2, phosphorene and silicene as shown in Table 2 [5,10,40–44]. Optimized structures of metal-functionalized BGDY under hydrogenation are given in Fig. 6.

For an ideal H2 storage material, in addition to a high content of H2 adsorption, desorption of H2 molecules at feasible operating conditions is of great importance. Thus, it is essential to investigate the desorption capacities of H2 under practical conditions of pressure and temperature. For this purpose, we have employed the thermodynamic analysis of the adsorption of H2 on light metal-doped BGDY monolayers for a given temperature and pressure to understand thermodynamics of H2. The number of H2 molecules can be calculated from the following formula [45,46].

\[
N_{H_2}(P, T) = N_0 \frac{\exp\left(\frac{\mu - \mu_0}{k_BT}\right)}{\sum \exp\left(\frac{\mu - \mu_n}{k_BT}\right)}
\]

where \(N_0\) denotes the maximum number of adsorbed H2 molecules, \(n\) indicates the number of H2 molecules, \(\mu\) denotes the chemical potential of the H2 gas, and \(\mu_0\) and \(\mu_n\) denote the adsorption energy per H2 molecule and degeneracy of the configuration, respectively. The chemical potential of H2 gas was used for the experimental values [47]. Using Eq. (4), the number of H2 molecules was calculated for BGDY@4X as shown in Fig. 7(a). The systems GBDY@4Li and BGDY@4Na require temperature lower than

<table>
<thead>
<tr>
<th>System</th>
<th>Type of study</th>
<th>Dopants</th>
<th>Hydrogen Storage Capacity (wt%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>Experimental</td>
<td>Pd</td>
<td>6.7</td>
<td>21</td>
</tr>
<tr>
<td>Graphene</td>
<td>Experimental</td>
<td>Ni</td>
<td>0.1–1.2</td>
<td>22</td>
</tr>
<tr>
<td>Graphyne</td>
<td>Theoretical (DFT)</td>
<td>Mg</td>
<td>10.6</td>
<td>23</td>
</tr>
<tr>
<td>Graphyne</td>
<td>Theoretical (DFT)</td>
<td>Li, Na</td>
<td>9–9.3</td>
<td>25</td>
</tr>
<tr>
<td>Graphdiyne</td>
<td>Theoretical (DFT)</td>
<td>Li, Na, K, Ca, Sc, Ti</td>
<td>4.91–6.5</td>
<td>5</td>
</tr>
<tr>
<td>Graphene</td>
<td>Theoretical (DFT)</td>
<td>Cu</td>
<td>4.23</td>
<td>4</td>
</tr>
<tr>
<td>C2N Sheets</td>
<td>Theoretical (DFT)</td>
<td>Li</td>
<td>10</td>
<td>41</td>
</tr>
<tr>
<td>MoS2</td>
<td>Theoretical (DFT)</td>
<td>Li</td>
<td>4.4</td>
<td>42</td>
</tr>
<tr>
<td>Phosphorene</td>
<td>Theoretical (DFT)</td>
<td>Li</td>
<td>5.3</td>
<td>43</td>
</tr>
</tbody>
</table>

Fig. 6. Top and side views of the optimized structures of (a–d) BGDY@4Ca and (e–h) BGDY@4Li loaded with 4 H2, 8 H2, 12 H2 and 16 H2, respectively. Brown, dark green, blue, light green, and red atoms represent C, B, Ca, Li and H, respectively. (A colour version of this figure can be viewed online.)
the others because the \( E_b \) values of H\(_2\) on Li and Na are smaller than that on K and Ca. In addition, the change of the number of H\(_2\) molecules is not linearly or parabolically, that is, there are multiple flat regions as the temperature decreases. This is ascribed to the fact that the adsorption is generated from the multiple binding energy of H\(_2\) according to the number of adsorbed H\(_2\) molecules. On the other hand, at higher pressure the adsorption occurs at a higher temperature as shown in Fig. 7(a) because the chemical potential of the H\(_2\) gas increases as the pressure increases \[48\]. Thus, the doped BGDY monolayer attains \( E_b \) storage capacities which are much higher than other 2D systems reported in the literature such as graphene, graphane, graphdiyne, graphyne, C\(_2\)N, g-C\(_3\)N\(_4\), h-BN, MXene, silicene, phosphorene. In order to design efficient H\(_2\) storage systems, which could operate under practical operating conditions of pressure and temperature, we have studied the thermodynamic properties of metal-doped BGDY monolayers. Our comprehensive thermodynamic analysis reveals that the H\(_2\) molecules adsorbed on the doped BGDY layer could be desorbed under practical conditions of pressure and temperature. Thus, metal functionalized BGDY is a promising material for efficient, reversible and high capacity H\(_2\) storage under ambient conditions applications.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2019.02.085.

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\(1\)


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