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1 **Boosting Hydrogen Storage Capacity in Modified-Graphdiyne Structures:**

2 **A Comprehensive Density Functional Study**

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27 **Abstract**

28 Graphdiyne (GDY) is a recently discovered two-dimensional carbon allotrope that holds
29 significant promise for applications in hydrogen adsorption and storage technology. This study
30 investigates the impact of nitrogen doping and sodium decoration on the hydrogen adsorption
31 capacity of GDY nanosheets while examining their influence on electronic and structural
32 properties. Various deliberate impurities are introduced to create modified-GDY structures.

33 Nitrogen doping triggers a transition from a semiconductor to a semi-metallic state, driven by
34 differences in electronegativity and adjustments in bond lengths. Cohesive energy (E_{coh}) is
35 found to be -7.231 eV for the most stable N-doped GDY. In contrast, sodium decoration
36 enhances conduction by modifying charge distribution. The other most stable structures are
37 Na-decorated GDY with E_{ads} of -3.804 eV and N, Na-decorated GDY with -3.347 eV.
38 Modified-GDY structures exhibit higher hydrogen adsorption energies compared to pristine
39 GDY, with N-doped GDY displaying the highest energy levels ($E_{\text{ads}} = -0.455\text{eV}$). Maximum
40 hydrogen adsorption capacities are assessed for each structure, and a notable improvement is
41 observed in Na-decorated GDY (19 H₂), significantly enhancing the storage capacity to 13.8
42 wt%, which shows a 10.21 wt% increase in H₂ adsorption compared to pure GDY (3.59 wt%).
43 These findings underscore the potential of modified-GDY for hydrogen storage applications,
44 highlighting the effectiveness of structural carbon modification in enhancing hydrogen
45 adsorption capacity.

46

47

48 **Keywords:** Graphdiyne, Hydrogen Storage, Adsorption, Nitrogen Doping, Sodium
49 Decoration, Density Functional Theory.

50 **1. Introduction**

51 In the present era of industrial expansion, the growing concern about greenhouse gas emissions
52 underscores the need for a deeper exploration of sustainable energy sources as alternative
53 solutions. It is imperative to adopt innovative approaches that can mitigate environmental
54 pollution, ensuring a sustainable future for generations to come [1]. Hydrogen (H₂) has
55 emerged as a promising energy carrier due to its clean properties, abundance, efficiency, eco-
56 friendliness, and economic sustainability [2]. However, the challenge of developing a compact
57 and efficient hydrogen storage system under ambient pressure conditions remains a significant
58 obstacle to achieving energy-efficient hydrogen-based energy generation [3].

59 In recent years, a wide array of materials, including nonporous solid media, has been rapidly
60 developed for use in hydrogen storage technologies [4]. Two-dimensional (2D) carbon-based
61 materials, such as graphene and its derivatives [5–7], have shown promise for H₂ storage due
62 to their high storage efficiency, as well as their chemical and thermal stability during the
63 hydrogen adsorption-desorption process [8,9]. Nevertheless, research findings have indicated
64 that pristine structures generally exhibit weak interactions with hydrogen, resulting in low
65 storage capacity [10,11]. Consequently, it becomes imperative to modify these structures to
66 enhance their interaction power and storage capacity, similar to the successful trapping of CO₂
67 gas [12,13].

68 Modifying nanomaterials by doping nonmetals or decorating metals is a common method to
69 increase efficiency in this domain [14]. 2D and 3D graphite systems containing heteroatoms
70 such as N, S, P, etc., can modify the thermal, mechanical, electronic, photonic, and surface
71 properties of the material. In this regard, energy devices made using robust N-doped structures
72 are very efficient in operation and very effective compared to pure systems [15]. Also, the
73 strategy of introducing diffuse excess electrons has been proposed to design new type of high-

74 performance materials based on molecules, even extending to carbon nanostructures. One of
75 these methods that leads to reducing the band gap and increasing the conductivity is decorating
76 the structures with alkali metals [16]. In the meantime, sodium (Na) has been chosen due to its
77 abundance and cost-effectiveness. In several studies, other metal and non-metal atoms like Al,
78 Ga, Mg, Zn, S, and B have been used as dopants on the structures of carbon nanotubes (CNT),
79 C60 and ZnO nanoparticles, and interesting results have been observed [17–20]. A recent study
80 on boron-substituted zeolite templated carbon vacancies for hydrogen adsorption found that
81 sodium decoration showed the best performance, allowing up to fifteen hydrogen molecules to
82 be adsorbed with a 6.55% wt storage capacity [21]. The Density Functional Theory (DFT)
83 method was employed to investigate the hydrogen storage potential of recently developed
84 graphene nanoflakes doped with chromium (Cr) atoms. Unlike pure graphene nanoflakes,
85 where H₂ molecules tended to migrate away from the surface, the Cr-doped graphene
86 nanoflakes exhibited a strong attraction to H₂, as indicated by a chemical adsorption energy of
87 -0.574 eV [22].

88 DFT calculations revealed that Mg-decorated graphyne, a graphene-based material, can
89 effectively store up to ten hydrogen molecules under the influence of an electric field. This
90 results in a remarkable hydrogen storage capacity of 10.64 wt% and an average adsorption
91 energy of -0.28 eV per H₂ molecule [23]. Akbari et al. investigated the impact of Al or N atom
92 doping on the electronic and structural properties of graphyne through DFT calculations [24].
93 Their study revealed that the introduction of these atoms altered the conductive nature of
94 graphyne from a semiconductor to a metallic state. According to their findings, these materials
95 can adsorb 4, 9, 7, and 16 H₂ molecules, respectively. Moreover, the hydrogen storage capacity
96 of Al-N co-doped graphyne can attain an impressive 16.67 wt%.

97 In 2010, Li et al. achieved the successful synthesis of graphdiyne (GDY) for the first time by
98 employing hexaethynyl benzene in a cross-coupling reaction on the surface of a copper (Cu)

99 foil [25]. GDY is a carbon allotrope consisting of hexagonal carbon rings connected by a
100 diacetylene bridge ($-C\equiv C-C\equiv C-$). Its structure encompasses sp and sp^2 hybridized carbon
101 atoms, with the $sp-sp^2$ hybridized carbon atoms serving as active sites [26]. Due to its unique
102 physicochemical properties, GDY has garnered significant attention for various applications,
103 spanning electronics, energy storage, electrode materials, lithium-ion batteries, photocatalysis,
104 drug delivery, CO_2 capture, and hydrogen purification [27–32].

105 As with other structures, several methods have been proposed in the literature to enhance the
106 reversible hydrogen storage capacity of GDY, including doping, decorating, and applying an
107 electric field [33,34]. For instance, Jiao et al. investigated nitrogen-modified GDY and its
108 potential for hydrogen purification from a $CH_4/CO/H_2$ mixture using DFT-D [29]. Their
109 findings indicated that nitrogen doping enhances hydrogen purification capabilities by reducing
110 the H_2 diffusion barrier and increasing the CH_4/CO diffusion barrier.

111 The addition of metal atoms to GDY can transform it from a small band-gap semiconductor to
112 a metallic state, with metal atoms in a partially positive state being desirable for reversible H_2
113 storage materials. Panigrahi et al. conducted a study on GDY decorated with light metals such
114 as Li, Na, K, Ca, Sc, and Ti (using the DFT-D3 method) to assess their potential for improving
115 reversible hydrogen storage capacity. They observed a capacity of 6.50 wt% for double metal-
116 decorated GDY [2]. The performance of Ca-decorated GDY in hydrogen storage was evaluated
117 using DFT-D2. According to this research, Ca-decorated GDY can adsorb 14 H_2 molecules on
118 each side of GDY with an average binding energy of approximately 0.2 eV, resulting in
119 hydrogen storage of 17.95 wt% [3].

120 Moreover, boron elements can modify Li and Na adsorption sites in graphdiyne, with double-
121 sided decorations exceeding bulk cohesive energies. The structures have estimated hydrogen
122 uptake capacities of 8.81 wt% and 7.73 wt%, while maintaining thermodynamic stability [35].

123 A study explored the effects of nitrogen (N) and sulfur (S) doping, as well as N and S co-
124 doping, on the structural and electrical properties of the GDY carbon structure. The
125 investigation also involved evaluating the H₂ adsorption and storage capacities of these
126 modified structures. The results demonstrated that the introduction of N and S dopants led to
127 significant variations in the adsorption energies of H₂ molecules. Additionally, the study
128 observed that charge injection had a notable impact on H₂ adsorption capacity. The findings
129 suggest that N and S doping, both individually and in combination, can effectively enhance the
130 H₂ storage capabilities of GDY nanosheets [36].

131 According to the aforementioned findings, the distinctive high π hybrid structure of GDY
132 results in a uniform nanohole distribution, nonuniform electron distribution, excellent electrical
133 conductivity, high electron mobility, tunable band gaps, and high chemical stability. These
134 properties render graphdiyne a promising material for high-performance products and a
135 potential solution for hydrogen storage.

136 In this study, we investigate the effects of individual nitrogen (N) and sodium (Na) atom doping
137 and decoration on the electronic and structural properties of GDY. Furthermore, we explore
138 the behavior of hydrogen adsorption on both pristine and modified GDY sheets, employing
139 DFT-D2 calculations. Our investigation delves into various carbon types and adsorption sites
140 within the GDY framework to pinpoint the optimal positions for N doping and Na decoration.
141 Subsequently, we systematically introduce H₂ molecules to the stable structures and analyze
142 the mean adsorption energy. To support these interactions, we utilize Hirshfeld charge analysis,
143 PDOS (Partial Density of States), and band structure diagrams to observe charge transfer
144 phenomena.

145

146

147 2. Computational methods

148 In this study, we optimized all configurations to investigate the impact of N-doping and Na-
149 decoration on the hydrogen storage capacity of the GDY structure. Geometry optimization was
150 carried out using the spin-polarized DFT method with the Perdew-Burke-Ernzerhof (PBE)
151 functional for exchange-correlation energy at the Generalized Gradient Approximation (GGA)
152 theory level [37].

153 For these calculations, we employed the DMol3 module [38] within the Materials Studio
154 software, utilizing the DNP basis set. This basis set offers accuracy comparable to the 6-31G
155 (d, p) basis set [39,40]. To account for dispersive intermolecular interactions and long-range
156 Van der Waals forces, we applied the DFT-D2 method developed by Grimme [41,42].

157 A $2 \times 2 \times 1$ supercell of the GDY unit cell was constructed, including a 20 \AA vacuum space in
158 the z-direction to prevent layer interactions. In the Brillouin zone, we employed a $7 \times 7 \times 1$
159 gamma-centered Monkhorst-Pack mesh for k-grid sampling. No symmetry constraints were
160 enforced during the geometry optimization process, and all atoms were allowed to relax.

161 To ensure accurate results, we set convergence tolerances as follows: energy tolerance of 10^{-5}
162 Ha, maximum force tolerance of $2 \times 10^{-3} \text{ Ha \AA}^{-1}$, displacement tolerance of $5 \times 10^{-3} \text{ \AA}$, and a
163 global orbital cut-off radius of 5.1 \AA .

164 Additionally, we calculated various parameters such as the band structure, density of states
165 (DOS), partial density of states (PDOS), charge density, and Hirshfeld (Mulliken) atomic
166 charges to qualitatively and quantitatively explain the results.

167 The stability of doped GDY structures can be assessed by calculating the cohesive energy (E_{coh})
168 using the following equation:

$$169 \quad E_{coh} = \frac{E_{D-GDY} - nE_C - mE_{dopant}}{n+m} \quad (1)$$

170 where E_{D-GDY} , E_C and E_{dopant} represent the total energy of the doped or decorated GDY structure
 171 with N or Na, isolated carbon, and dopant (N or Na) atoms, respectively. In this equation, n
 172 and m denote the numbers of carbon and dopant atoms in the modified GDY, respectively

173 The average adsorption energy (E_{ads}) and consecutive adsorption energy (E_s) per H_2 molecule
 174 were calculated using the following equations:

$$175 \quad E_{ads} = \frac{E_{nH_2+D-GDY} - E_{D-GDY} - nE_{H_2}}{n} \quad (2)$$

$$176 \quad E_s = E_{nH_2+D-GDY} - E_{(n-1)H_2+D-GDY} - E_{H_2} \quad (3)$$

177 In these equations, $E_{nH_2+D-GDY}$ represents the total energy of the complex containing doped
 178 GDY and n H_2 molecules, $E_{(n-1)H_2+D-GDY}$ is the total energy of the complex containing doped
 179 GDY and (n-1) H_2 molecules, E_{D-GDY} is the total energy of doped GDY, and E_{H_2} represents the
 180 energy of an isolated H_2 molecule. Here, 'n' signifies the number of adsorbed hydrogen
 181 molecules. The adsorption energy of the *n*th H_2 molecule onto the previous structure is denoted
 182 as E_s . When the value of this energy falls below 0.1 eV, it serves as a criterion to cease the
 183 addition of hydrogen. This threshold indicates that the adsorbent is not sufficiently suitable for
 184 the adsorption of the *n*th hydrogen molecule.

185 The hydrogen storage capacity is determined using the following equation:

$$186 \quad H_2 \text{ storage capacity (wt\%)} = \frac{M_{H_2}}{M_{H_2} + M_{sheet}} \times 100 \quad (4)$$

187 where M_{H_2} represents the mass of adsorbed H_2 , and M_{sheet} represents the mass of the host
 188 material.

189

190 **3. Results and discussion:**

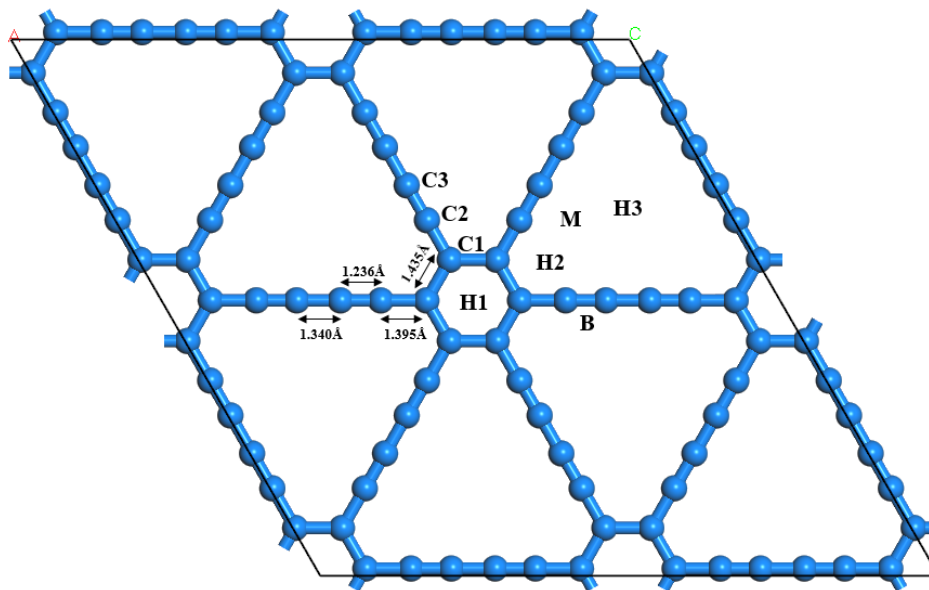
191 **3.1. Assessment of the structural and electronic properties of pristine and modified-GDYs**

192 Fig. 1 displays the top view of the GDY supercell. The lattice parameters employed in all
193 calculations were determined as follows: $a = b = 18.94 \text{ \AA}$, $c = 20 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$.
194 The GDY structure exhibits a symmetric composition, comprising a sp^2 -hybridized hexagonal
195 carbon ring and six sp -hybridized acetylenic carbon chains [43]. The structure encompasses
196 three distinct types of carbon atoms: C1 ($C_{sp^2-sp^2}$), C2 (C_{sp^2-sp}), and C3 (C_{sp-sp}), each
197 characterized by different hybridizations. The connection of these carbon variants results in the
198 formation of four types of bonds, each with bond lengths measuring 1.435, 1.395, 1.236, and
199 1.340 \AA . The 2×2 supercell of GDY comprises 72 carbon atoms. The findings indicate that this
200 nanostructure exhibits a semiconductor nature with a band gap of 0.44 eV at the gamma point.
201 It's important to note that different computational conditions in theoretical studies may yield
202 varying values for the band gap [3,44]. Furthermore, the GDY system lacks inherent spin
203 polarization or magnetism due to identical spin-up and spin-down bands. Consequently, the
204 results from the GDY structure optimization are consistent with previous research findings
205 [40,45].

206 Three types of non-equivalent carbon atoms were replaced with nitrogen atoms, and the
207 resulting structures were subsequently optimized. Remarkably, the substitution of a nitrogen
208 atom for the C2 carbon atom resulted in the formation of the most stable structure among the
209 modified configurations, as indicated by its cohesive energy (E_{coh}) of -7.231 eV.

210 In the subsequent investigation of the impact of sodium (Na) metal decoration on the GDY
211 structure, Na atoms were placed at different positions on the GDY plane (H1, H2, H3, and B)
212 and at varying distances (d). As shown in Table 1, it becomes evident that when the Na atom
213 is positioned directly on the GDY plane ($d=0$) at the H3 site, it results in the most stable
214 decorated GDY structure, accompanied by an adsorption energy (E_{ads}) of -3.804 eV. Upon
215 decorating the Na atom at various sites on the most stable N-doped GDY structure, it is
216 discernible from Table 1 that the H3 site consistently exhibits the highest stability among the

217 simultaneously doped and decorated structures. The adsorption energy at the H3 site is
 218 recorded as -3.347 eV.



219 **Fig. 1.** The optimized structures of pristine GDY with various C-C bond lengths, three types of C atoms and five
 220 considered sites are labeled as C1-C3 and H1-H3, B, and M, respectively.

221

222 **Table 1.** Binding energies and adsorption energies of modified GDYs (N doped, Na decorated, and N doped Na
 223 decorated) structures at different binding and adsorption sites.

Structure	Cohesive Energy (eV)			Adsorption energy(eV)						
	C1	C2	C3	H1		H2		H3		B
				d(Å)=0	d(Å)=1.5	d(Å)=0	d(Å)=1.5	d(Å)=0	d(Å)=1.5	
N-GDY	-7.216	<u>-7.231</u>	-7.226	--	--	--	--	--	--	--
Na-GDY	--	--	--	-2.986	-2.963	-3.803	-3.802	<u>-3.804</u>	-3.797	-3.502
N, Na-GDY	--	-7.231	--	-2.759	-2.759	-3.346	-3.344	<u>-3.347</u>	-3.344	-3.334

224

225 In the subsequent sections of this paper, the most stable configurations of pure GDY, N-GDY,
 226 Na-GDY, and N, Na-GDY structures have been designated as S1, S2, S3, and S4, respectively.

227 Table 2 presents the bond lengths, cohesive energies, bandgap energies (E_g), and Fermi levels
 228 (E_f) for these stable structures. The optimized geometrical structures are depicted in Fig. 2,
 229 providing both top and side views.

230

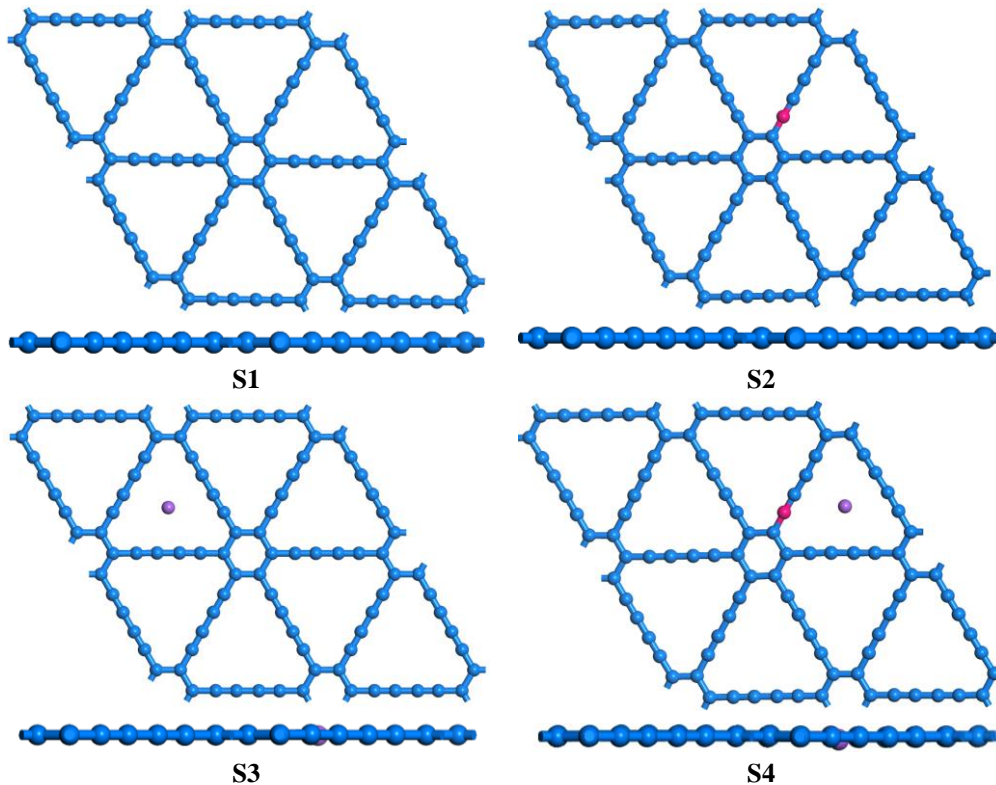
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232 **Table 2.** Structural and electronic properties of pristine GDY and best conformations of the modified GDYs.

Structure	C1-C1 (Å)	C1-C2 (Å)	C2-C3 (Å)	C3-C3 (Å)	E_{coh} (eV)	E_{ads} (eV)	E_g (eV)	E_f (eV)
(S1)	1.236	1.395	1.435	1.340	-7.266	-	0.445	-5.223
(S2)	1.197	1.347	1.438	1.323	-7.231	-	0.000	-4.906
(S3)	1.239	1.394	1.435	1.339	-7.219	-3.804	0.000	-4.850
(S4)	1.209	1.339	1.439	1.315	-7.178	-3.347	0.000	-4.841

233

234



235 **Fig. 2.** The optimized geometrical structure of Pristine GDY (S1), N-GDY (S2), Na-GDY (S3), and N, Na-
 236 GDY (S4). (The blue, dark pink and purple balls represent C, N, and Na atoms, respectively.)

237

238 The introduction of nitrogen (N) into the GDY framework brings about both structural and
 239 electronic effects. The smaller size of the N atom and its higher electronegativity in comparison
 240 to carbon (C) can induce changes in the bond lengths of neighboring atoms. As depicted in
 241 Table 2, there is a reduction in the lengths of $C_{\text{sp}2}\text{-}C_{\text{sp}}$ and $C_{\text{sp}}\text{-}C_{\text{sp}}$ bonds, accompanied by an
 242 increase in $C_{\text{sp}2}\text{-}C_{\text{sp}2}$ bond length. The replacement of C with N results in the formation of N-
 243 C bonds, causing alterations in electron distribution, which, in turn, impacts the total energy of
 244 the structure.

245 The band structure diagrams for the S1-S4 structures are displayed in Fig. 3, with the Fermi
246 level set at zero. Notably, the band gap of N-GDY undergoes a transformation, decreasing from
247 0.445 eV to zero. This transition signifies a shift from a semiconductor to a semi-metallic
248 nature. The modification of the GDY structure results in an elevation of the Fermi level,
249 moving closer to the conduction band. This observation suggests that the modified structures
250 exhibit n-type semiconductor characteristics or improved semi-metallic properties, in
251 alignment with prior reports for graphyne. The S4 structure exhibits the most notable shift in the
252 Fermi level, confirming its higher conductivity compared to the other modified structures. While pure
253 GDY displays characteristics of a direct semiconductor, the introduction of nitrogen (N-GDY) and
254 sodium (Na-GDY) induces alterations in the electron band structure, resulting in a complete overlap of
255 the conduction bands with the Fermi energy level.

256 The electrical conductance is exponentially related to the bandgap (E_{gap}), with conductivity
257 increasing as E_{gap} decreases. The difference between the highest occupied molecular orbital
258 (HOMO) and the lowest unoccupied molecular orbital (LUMO) can be used to estimate the
259 E_{gap} value, which, in turn, is linked to electric conductance through the formula [46]:

$$260 \quad \sigma \propto e^{\frac{-E_{\text{gap}}}{kT}} \quad (5)$$

261 where σ represents electrical conductance, k is Boltzmann's constant, and T denotes absolute
262 temperature. This relationship highlights a fundamental aspect of semiconductor behavior:
263 conductivity increases as the bandgap decreases. Lower band gaps result in higher
264 conductance, a principle that is crucial in understanding the electrical properties of materials.

265 We have specifically applied this concept to our study on GDY. Our analysis (Table 2 and Fig.
266 3) reveals that GDY exhibits semiconductor behavior with a direct band gap of 0.445 eV at the
267 gamma point (S1), a value consistent with recent research findings [40]. In modified GDY
268 structures (S2, S3, and S4), alterations in the band gap are observed, leading to shifts in the

269 conduction bands relative to the Fermi level. This phenomenon results in a transformation of
270 GDY from a semiconductor to a semi-metallic state.

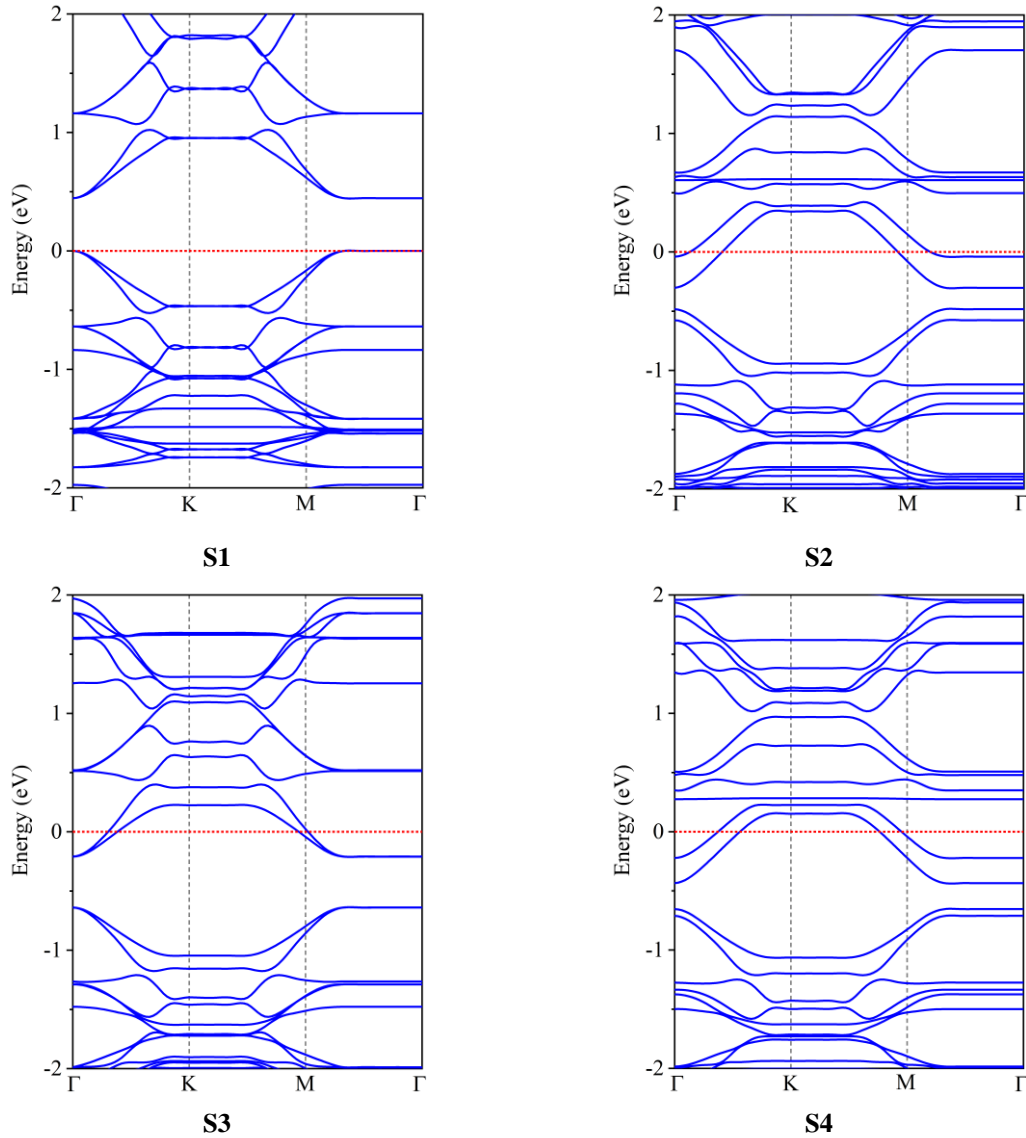
271 Understanding the relationship between bandgap and electrical conductance is essential not
272 only for characterizing materials like GDY but also for predicting their behavior under various
273 conditions. For instance, in our study, we investigated the influence of hydrogen molecules
274 during adsorption processes. Such insights are invaluable for the design and optimization of
275 materials for specific applications where electrical conductivity is a critical factor.

276 In summary, the formula for electrical conductance provides a quantitative framework for
277 elucidating the electronic properties of materials, thereby facilitating informed decision-
278 making in material design and engineering.

279 In the S2 structure, Hirshfeld charges of neighboring N atoms, specifically C1 and C3, have
280 undergone a significant change, transitioning from $0.023 e^-$ and $0.013 e^-$ to $0.062 e^-$ and 0.134
281 e^- , respectively. This shift indicates a transfer of electron density to the N atom, resulting in a
282 Hirshfeld charge of $-0.004 e^-$ for the N atom. Consequently, the introduction of the N atom
283 disrupts the electric charge symmetry of the structure.

284 Furthermore, the presence of Na metal in the GDY structure induces charge transfer to the C
285 atoms, with the Na atom carrying a positive charge of $+0.482$. In the S4 structure, the charge
286 transfer from the Na metal to the electronegative N atom results in a more negative charge for
287 the N atom compared to the S3 structure (refer to Fig. 4).

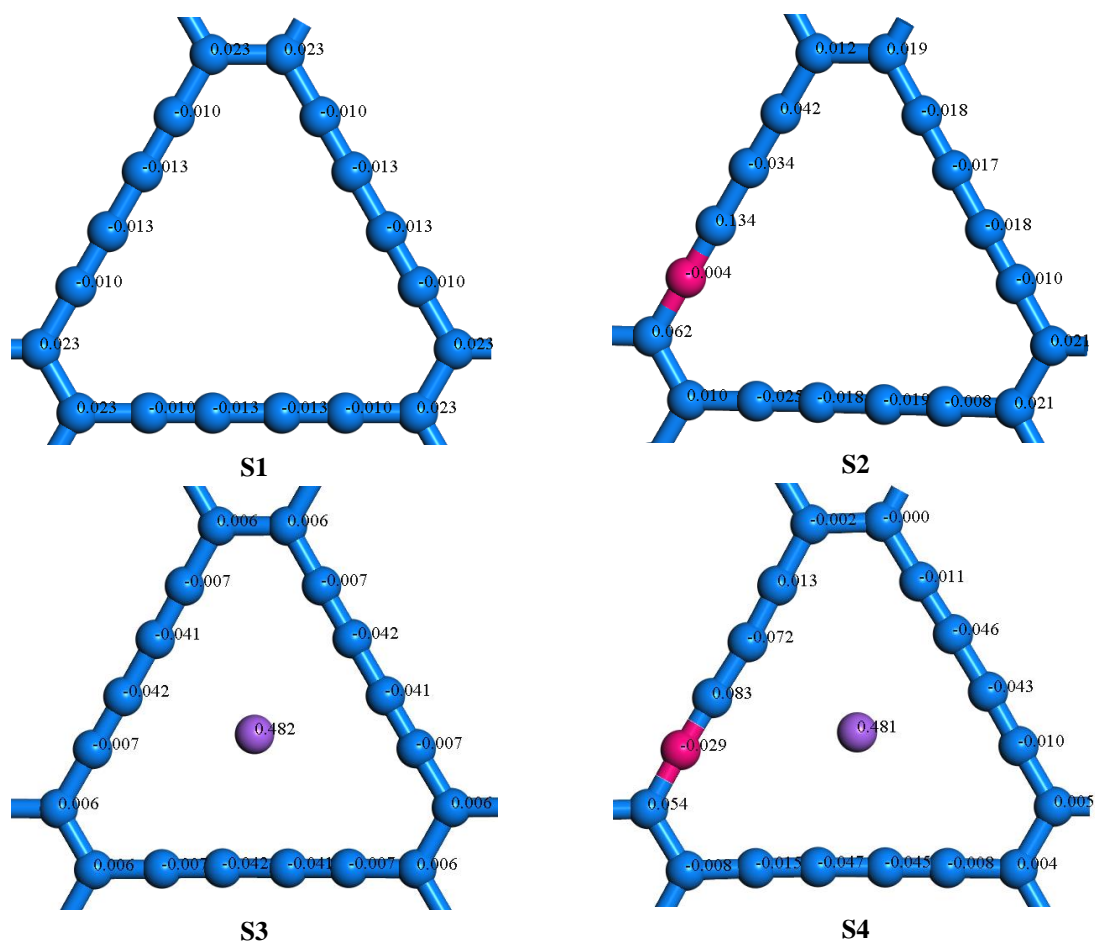
288 Figure 5 presents the Total Density of States (TDOS) and Projected Density of States (PDOS)
289 diagrams for the S1 to S4 structures. Analyzing the Density of States (DOS) offers valuable
290 insights into the bonding mechanisms, atom interactions, hybridization, and the effects of
291 charge transfer.



292 **Fig. 3.** Band structure of (S1) pristine GDY, (S2) N-GDY, (S3) Na-GDY and (S4) N, Na-GDY. The Fermi level
 293 was set to zero.

294 A comparison of the PDOS diagrams between pristine GDY (S1) and N-doped GDY (S2)
 295 reveals an increase in the contribution of s and p orbitals around the Fermi energy. This increase
 296 can be attributed to the higher number of electrons in the p orbital of the N atom introduced in
 297 the N-doped GDY structure. The introduction of N as an impurity enhances the electron density
 298 at energy levels above the Fermi level, which plays a crucial role in electrical conductivity and
 299 the transition of the structure from a semiconductor to a semi-metallic state.

300



302 **Fig. 4.** Hirshfield charges of C, N, and Na atoms in pristine (S1), N-GDY (S2), Na-GDY (S3), and N, Na-GDY
 303 (S4).

304

305 The charge density distribution in the s orbital for GDY spans the energy range of -6 to -20 eV,
 306 while for N-doped GDY, it extends from -6 to -22 eV. Overall, in the N-doped GDY structure,
 307 there is a shift in electron density towards lower energy levels, and the transfer of electric
 308 charge from the N orbitals to the anti-bonding orbital of the carbon atoms leads to an increased
 309 charge density at energy levels above the Fermi level.

310 In the PDOS analysis of the S3 structure, the charge distribution and density within the s orbital
 311 remained relatively stable when compared to the pristine GDY structure. However, a notable
 312 shift in charge distribution towards higher energy levels occurred upon Na decoration.

313 Additionally, the charge distribution in the conduction band exhibited an increase in the
314 decorated structure in contrast to the pristine GDY structure.

315 Within the S3 structure, the carbon atoms featuring sp^2 - sp^2 hybridization displayed a decrease
316 in charge density within the π orbital, while the charge density in the π^* orbital increased. This
317 observation is likely a result of charge transfer from the Na metal to this anti-bonding orbital.
318 Furthermore, the charge density in the p and s orbitals of the C_{sp} - C_{sp} atom decreased, and the
319 charge density distribution spanned a wider range of energy levels.

320 Analysis of the PDOS also revealed a low charge density in the Na orbitals, consistent with the
321 anticipated electronic charge of the Na atom. Consequently, Na contributed additional
322 electronic charge to the atoms of the GDY structure. The elevation of the Fermi level led to a
323 downward shift in the conduction band, facilitating conduction within the structure.

324 By examining the TDOS and PDOS diagrams of the pristine GDY structure following the
325 introduction of N and Na (S4), we can assess the combined effects. In the TDOS diagram, the
326 p orbital displayed an increased charge density due to N doping. This implies that the presence
327 of Na metal, akin to N doping, has led to an augmentation in the electron population within the
328 p orbital at energy levels beyond the Fermi level.

329 When comparing the PDOS diagrams of carbon atoms, noticeable changes were observed. The
330 π^* orbital of the carbon atom featuring sp^2 - sp hybridization exhibited the most significant
331 alteration in charge density, while the π orbital of the C_{sp} - C_{sp} carbon atom experienced the
332 highest increase. This observation suggests that the electric charge donated by Na metal atoms
333 tends to accumulate in the bonded orbitals of C_{sp} - C_{sp} and non-bonded orbitals of C_{sp^2} - C_{sp}
334 carbon atoms.

335 In summary, the incorporation of N and Na into the GDY structure results in discernible effects.
336 The TDOS diagram indicates an increase in charge density in the p orbital, signifying enhanced
337 electron population above the Fermi level. Furthermore, the PDOS analysis reveals that the

338 charge density changes predominantly occur in the π^* orbital of carbon atoms with sp^2 - sp
 339 hybridization and the π orbital of C_{sp} - C_{sp} carbon atoms. These findings suggest that the
 340 electrical charge donated by Na metal atoms tends to be concentrated in specific carbon orbitals
 341 within the GDY structure.

342

343 3.2. Adsorption of single H_2 molecule onto the pristine and modified-GDYs

344 Subsequently, we proceeded to investigate the adsorption of a single H_2 molecule on both the
 345 pristine GDY (S1) and modified-GDY structures (S2, S3, and S4). We explored various
 346 positions around the nanosheets, both horizontally and vertically, and assessed the adsorption
 347 energy. Fig. 6 depicts the most stable configurations of H_2 adsorption on the pristine GDY and
 348 modified GDY structures. Table 3 provides the results concerning H_2 adsorption on different
 349 sites (H1, H2, H3, B, and M) of S1-S4 structures in both the vertical (V) and horizontal (H)
 350 directions.

351 It is noteworthy that the modified structures exhibited a greater capacity to adsorb H_2 compared
 352 to the pristine structure, indicating an enhancement in adsorption properties due to the
 353 introduced modifications. Among all the modified structures, the S2 structure displayed the
 354 most favorable adsorption properties, primarily due to its higher adsorption energy.

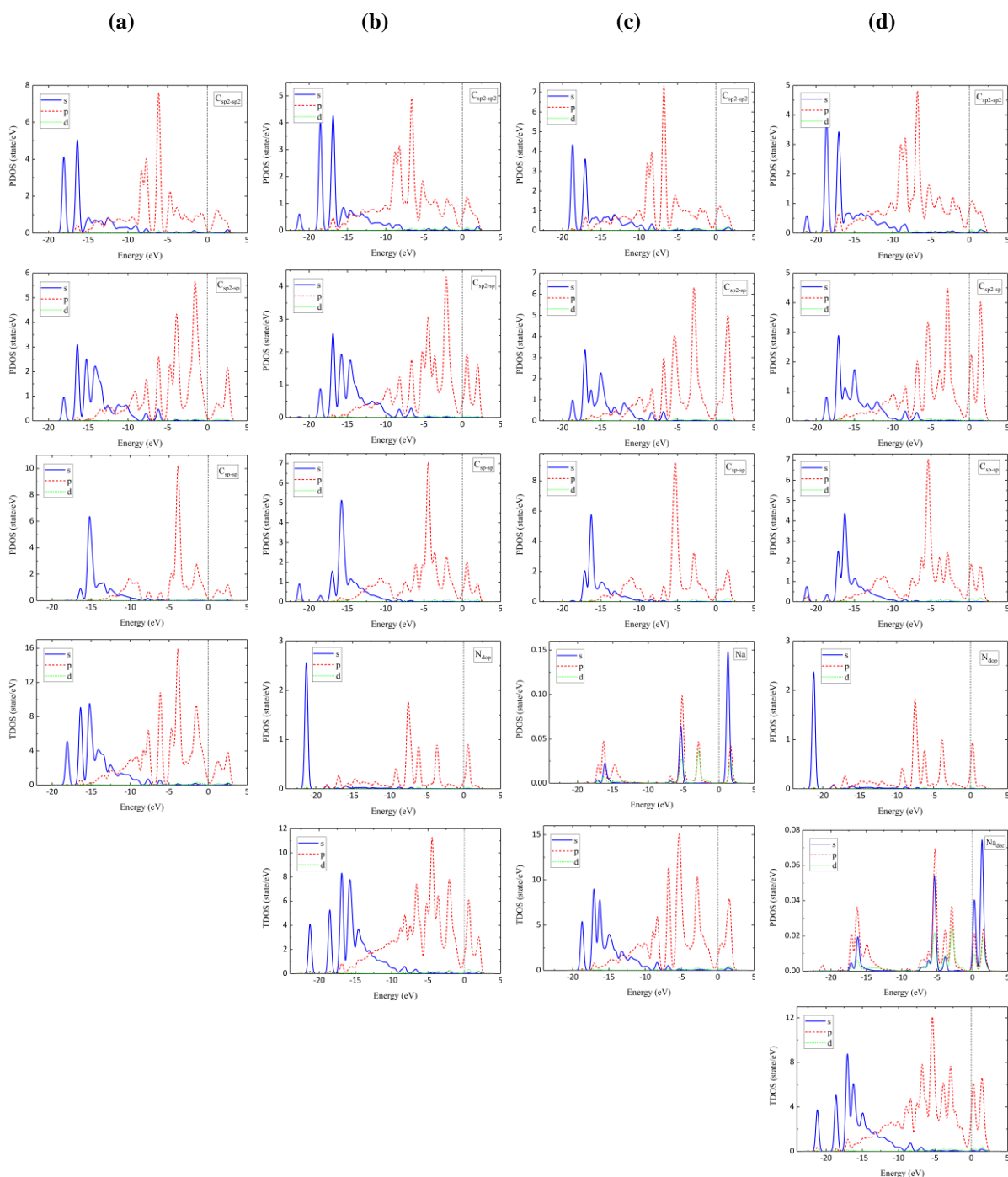
355

356 **Table 3.** Adsorption energy of single adsorbed H_2 on the pristine and the modified GDY at different considered
 357 sites.

Structure	Adsorption energy(eV)									
	H1		H2		H3		B		M	
	V	H	V	H	V	H	V	H	V	H
S1	-0.167	-0.187	-0.176	-0.166	-0.185	<u>-0.204</u>	-0.159	-0.161	--	--
S2	-0.131	-0.128	-0.126	-0.442	-0.133	<u>-0.455</u>	-0.111	-0.112	--	--
S3	-0.161	-0.148	-0.285	-0.287	-0.270	<u>-0.289</u>	-0.110	-0.184	--	--
S4	-0.153	-0.148	-0.283	-0.284	-0.280	-0.281	-0.130	-0.148	-0.135	<u>-0.286</u>

358

359



360 **Fig. 5.** TDOS and PDOS diagrams related to (a) S1, (b) S2, (c) S3, and (d) S4.

361

362 As indicated in Table 3, H3 emerges as the most favorable location for H₂ adsorption on
 363 structures S1, S2, and S3, while M proves to be the optimal adsorption site for S4, positioned
 364 between H3 and the C2 atom's location. Table 4 provides information on the adsorption energy,
 365 H-H bond length, and charge associated with each H, N, and Na atom for all systems.

366 The calculated bond length and angle for a free H₂ molecule stand at 0.748 Å and 180.0°,
 367 respectively. However, as the H₂ molecule adsorbs onto the S1-S4 structures, the H-H bond
 368 length experiences an increase, with the maximum value observed in the S4 structure at 0.752
 369 Å.

370

371 **Table 4.** Adsorption energy (E_{ads}) of single adsorbed H₂, H–H bond length ($L_{\text{H-H}}$), and the charge of H in H₂
 372 molecule, and the charges of N and Na atoms (e) in S1-S4 structures.

Structure	E_{ads}	$L_{\text{H-H}}$	Hirshfeld charges (e)			
			H	H	N	Na
S1	-0.204	0.751	-0.023	-0.021	-	-
S2	-0.455	0.751	-0.022	-0.014	-0.003	-
S3	-0.289	0.751	0.024	0.023	-	0.434
S4	-0.286	0.752	0.020	0.019	-0.028	0.436

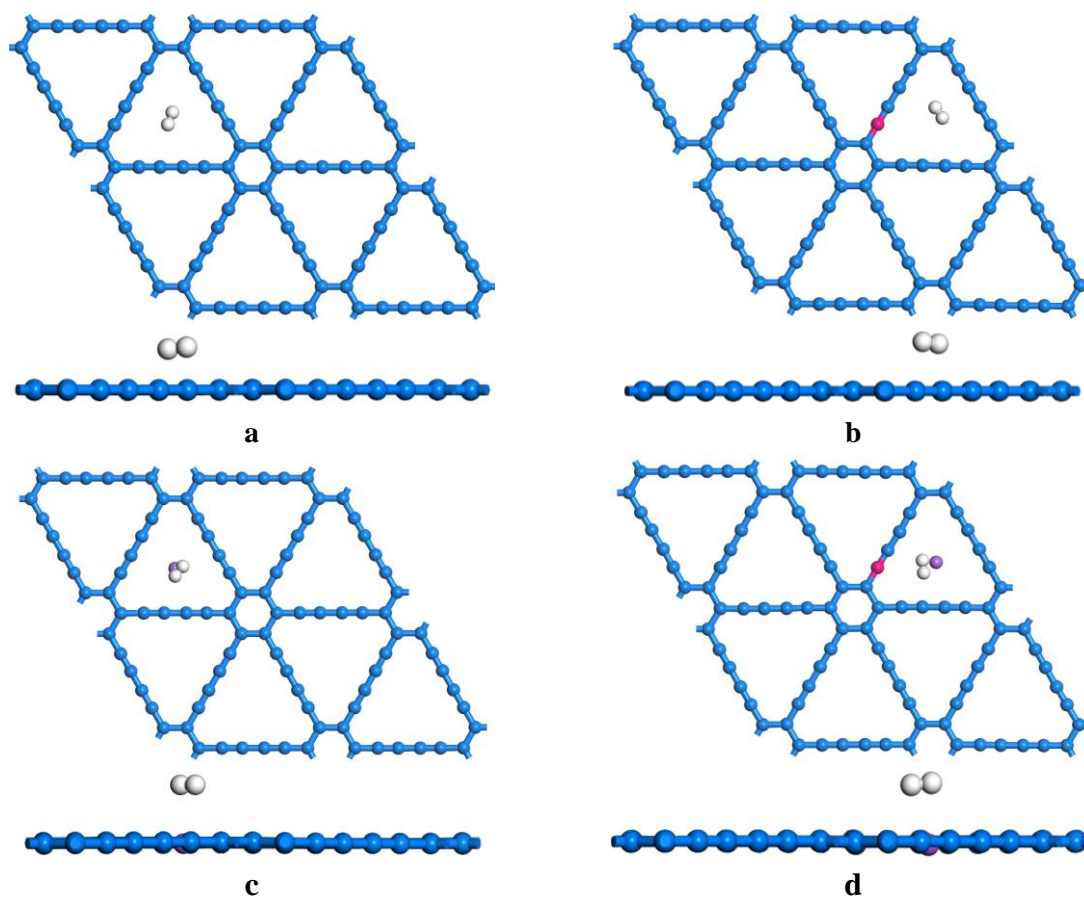
373

374 Furthermore, in Fig. 7, the electrical charge distribution of each atom is depicted. It is clear that
 375 the electrical charge of the hydrogen molecule atoms varies across different structures, leading
 376 to energy variations and exerting an influence on the overall structural stability. This energy
 377 discrepancy arises from differences in Coulombic energy and subsequently affects the
 378 adsorption energy, consequently influencing the structural stability of the systems.

379 The PDOS diagrams in Fig. 8 provide insights into the interactions between hydrogen and the
 380 pristine and modified GDY structures. These diagrams illustrate the contribution of each type
 381 of structural carbon atom, modifier atoms (N, Na), and H₂ in various states. For the S1 structure,
 382 the PDOS reveals a weak interaction between the H₂ molecule and pristine GDY, which is
 383 consistent with observations in other structures [10,11]. This is primarily due to the low
 384 contribution of C atoms in the bonding orbitals around -5 eV.

385

386



387 **Fig. 6.** Top and side views of the most stable sites and orientation of the H₂ adsorption on (a) S1, (b) S2, (c) S3,
 388 and (d) S4 structures.

389

390 In the case of the N-GDY system, when the C1 atom is replaced with N in the S2 and S4
 391 structures, the PDOS diagram displays a noteworthy interaction between the N atom and the C
 392 atoms in the GDY sheet. Specifically, the peaks of the N atom and the p-orbitals of the GDY
 393 sheet's C atoms exhibit effective hybridization. This interaction is observed in the energy range
 394 of -4 to -8 eV, where the N(p) peaks align with the C(p) peaks, as well as in the vicinity of the
 395 Fermi level. As a result, a strong N-bond is formed within the GDY structure.

396

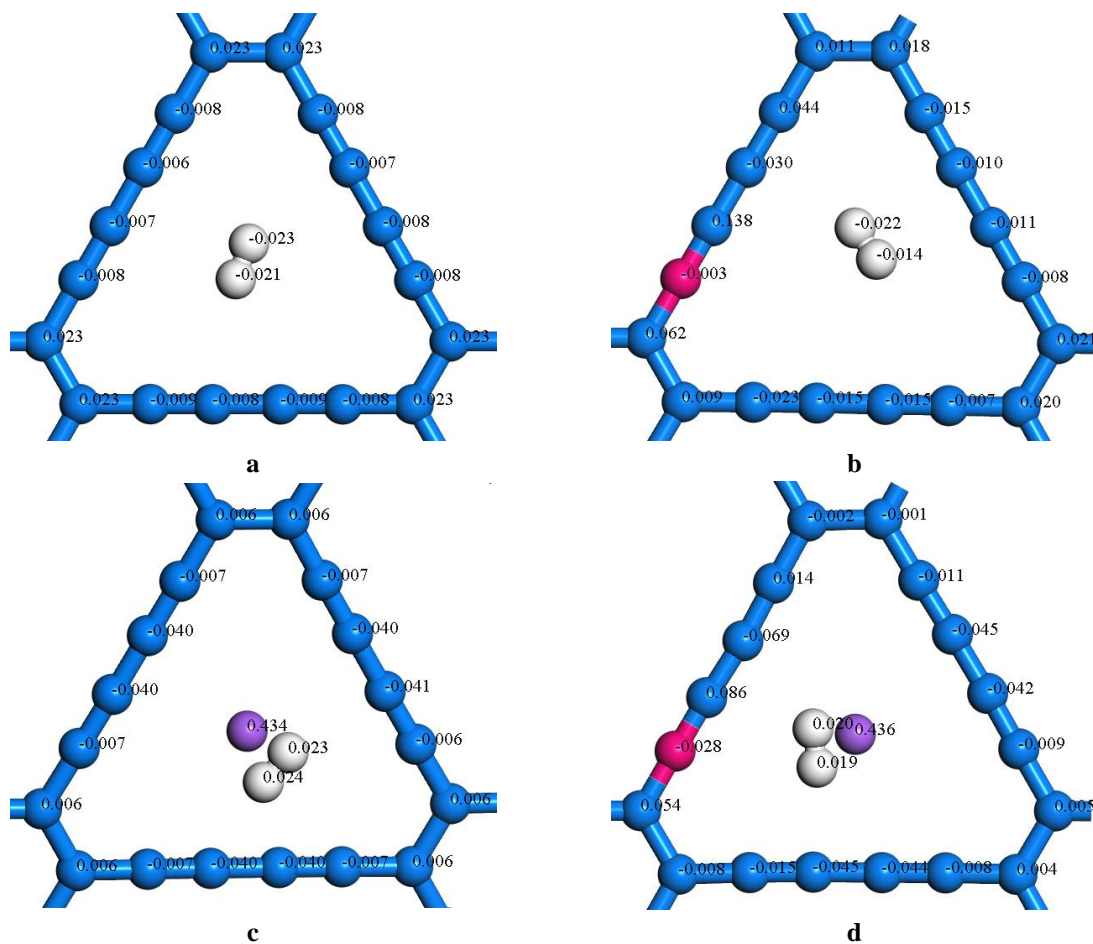
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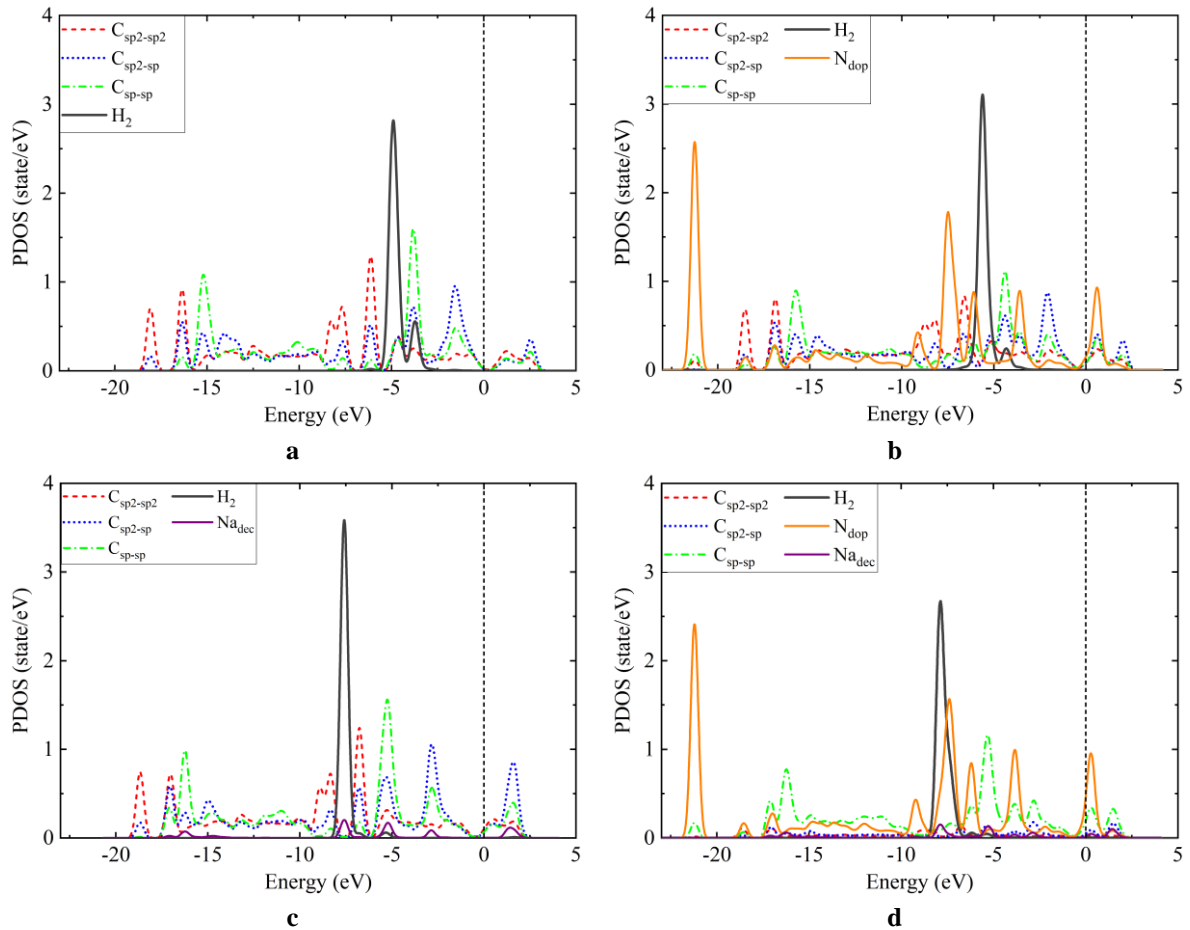
402 **Fig. 7.** The atomic Hirshfeld charges in the H₂ adsorbed structures: (a) S1 (b) S2, (c) S3, and (d) S4

403

404 Due to the N atom's surplus electrons compared to the C atom, the introduction of N into the
 405 GDY lattice leads to an increase in electron density within the valence band. This results in the
 406 presence of additional electron-filled states near the lower conduction bands, facilitating the
 407 easy transition of electrons into the conduction band. Essentially, the extra valence electron
 408 originating from the N atom's 2p orbital contributes to the GDY π^* state.

409 In the PDOS diagrams, it becomes evident that the interaction between the N atom's p orbitals
 410 and the H₂ molecule is stronger compared to the interaction between the Na metal orbital and
 411 the H₂ molecule (between -5 to -10 eV) in S3 and S4 structures. As a result, the adsorption of
 412 the hydrogen molecule on the S2 structure is more pronounced than on the S3 and S4 structures.
 413 This is further supported by the adsorption energy value of -0.455 eV, confirming the stronger

414 interaction. Therefore, it can be concluded that the overlap of orbitals between the H₂ molecule
 415 and the adsorbent, observed in the PDOS of modified structures, can improve the adsorption
 416 of H₂ gas molecules.

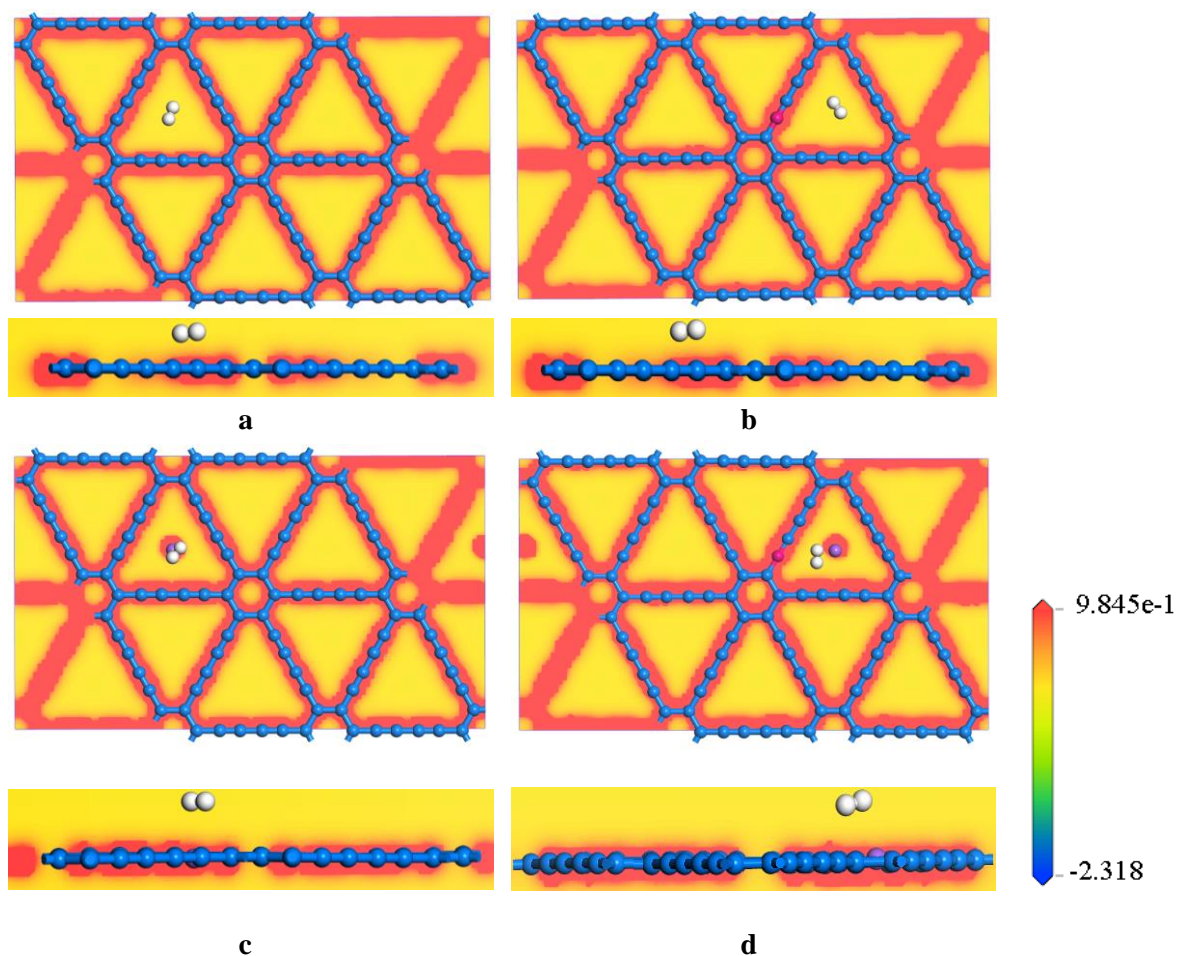


417 **Fig. 8.** The PDOS diagrams of the H₂ adsorbed onto: (a) S1, (b) S2, (c) S3, and (d) S4 structures.

418

419 Fig. 9 presents the electron density distribution for each structure, with yellow and red sections
 420 denoting depleted and enhanced electron areas, respectively. An intriguing observation is that
 421 the introduction of Na into the 18-ring structure results in the accumulation of electrons in a
 422 specific region. This electron accumulation has the potential to generate an electric field within
 423 the GDY structure, which could be a contributing factor to the enhanced performance of the
 424 S3 and S4 structures in terms of H₂ adsorption.

425



426 **Fig. 9.** The difference electron density images of adsorbed H₂ onto (a) S1, (b) S2, (c) S3, and (d) S4 structures.

427

428 3.3. Storage

429 To determine the optimal performance of a structure, hydrogen storage capacity plays a crucial
 430 role. To evaluate the maximum adsorption capacity of each structure, H₂ molecules were
 431 progressively added, and the systems were optimized at each step to obtain the total adsorption
 432 energy (E_{ads}) and the adsorption energy at each incremental addition (E_s). The United States
 433 Department of Energy has defined an optimal range for hydrogen uptake, which serves as a
 434 performance benchmark. Table 5 provides data on the average adsorption energy, adsorption
 435 energy at each incremental step, H-H bond length, and hydrogen storage capacity (wt%) for
 436 S1-S4 structures.

437 Initially, the bond length of the H₂ molecule measures 0.748 Å. However, as the process of
438 hydrogen uptake and storage proceeds, the bond lengths of all H₂ molecules increase, falling
439 within the range of 0.750 to 0.752 Å. The adsorption capacity of the H₂ molecule for structures
440 S1, S2, S3, and S4 is found to be 4, 12, 19, and 19 H₂ molecules, respectively. In Fig. 10, the
441 structures S1-S4 with maximum H₂ absorption are depicted.

442 The calculated weight percentages for structures S1, S2, S3, and S4 are determined as 3.59%,
443 9.98%, 13.80%, and 13.70%, respectively. These values are comparable to those reported in
444 other studies involving modified structures [24,34,36]. The introduction of N atoms into the
445 structure significantly enhances the storage capacity of H₂. Furthermore, the inclusion of Na in
446 structures S1 and S2 results in a threefold increase in the adsorption capacity compared to that
447 of S1. While structures S3 and S4 accommodate the same number of H₂ molecules, the higher
448 weight of structure S4 results in a slightly lower weight percentage than that of structure S3.
449 Consequently, it can be inferred that structure S3 exhibits greater storage efficiency, achieved
450 simply by incorporating Na within GDY.

451 The introduction of Na atoms into the structure creates an electron accumulation zone,
452 enhancing the electric field, in addition to the existing field in the pristine structure. This
453 phenomenon influences the storage of H₂ molecules, leading to a higher accumulation of H₂
454 within the adsorption region. Fig. 11 provides a comparison between the average adsorption
455 energy (in eV) and the number of adsorbed H₂ molecules for both pristine and modified GDY
456 nanosheets.

457

458

459

460 **Table 5.** The average adsorption energy (E_{ads}), consecutive adsorption energy (E_s), H-H bond length ($L_{\text{H-H}}$) and
 461 maximum H_2 adsorption capacity (wt. %) for various number of H_2 molecules and for S1-S4 configurations.

Struc.	#H ₂	E_{ads}	E_s	$L_{\text{H-H}}$	Wt. %	Struc.	#H ₂	E_{ads}	E_s	$L_{\text{H-H}}$	Wt. %	Struc.	#H ₂	E_{ads}	E_s	$L_{\text{H-H}}$	Wt. %
S1	1	-0.204	-0.204	0.751	3.59%	S3	1	-0.288	-0.287	0.751	13.8%	S4	1	-0.286	-0.286	0.752	13.7%
	2	-0.190	-0.177	0.751			2	-0.288	-0.287	0.751			2	-0.288	-0.290	0.752	
	3	-0.170	-0.129	0.751			3	-0.237	-0.137	0.751			3	-0.273	-0.243	0.752	
	4	-0.159	-0.128	0.751			4	-0.216	-0.152	0.751			4	-0.235	-0.123	0.751	
	5	-0.139	-0.059	0.751			5	-0.207	-0.170	0.751			5	-0.232	-0.220	0.750	
S2	1	-0.455	-0.289	0.751	9.98%	6	-0.198	-0.151	0.751	6	-0.221	-0.164	0.750				
	2	-0.298	-0.287	0.751		7	-0.197	-0.195	0.751	7	-0.210	-0.142	0.750				
	3	-0.248	-0.137	0.751		8	-0.189	-0.133	0.751	8	-0.202	-0.150	0.750				
	4	-0.221	-0.152	0.751		9	-0.182	-0.129	0.750	9	-0.197	-0.155	0.751				
	5	-0.204	-0.170	0.752		10	-0.178	-0.133	0.751	10	-0.191	-0.134	0.751				
	6	-0.194	-0.151	0.751		11	-0.176	-0.162	0.751	11	-0.186	-0.144	0.751				
	7	-0.190	-0.195	0.751		12	-0.173	-0.138	0.751	12	-0.181	-0.123	0.751				
	8	-0.184	-0.133	0.751		13	-0.170	-0.134	0.750	13	-0.179	-0.154	0.751				
	9	-0.178	-0.129	0.752		14	-0.170	-0.171	0.751	14	-0.177	-0.154	0.751				
	10	-0.174	-0.133	0.751		15	-0.166	-0.113	0.751	15	-0.174	-0.131	0.750				
	11	-0.171	-0.162	0.750		16	-0.163	-0.111	0.751	16	-0.173	-0.150	0.751				
	12	-0.166	-0.138	0.750		17	-0.160	-0.124	0.751	17	-0.169	-0.117	0.750				
	13	-0.160	-0.086	0.750		18	-0.158	-0.114	0.751	18	-0.170	-0.180	0.751				
						19	-0.156	-0.124	0.751	19	-0.170	-0.169	0.751				
						20	-0.153	-0.096	0.750	20	-0.165	-0.067	0.748				

462

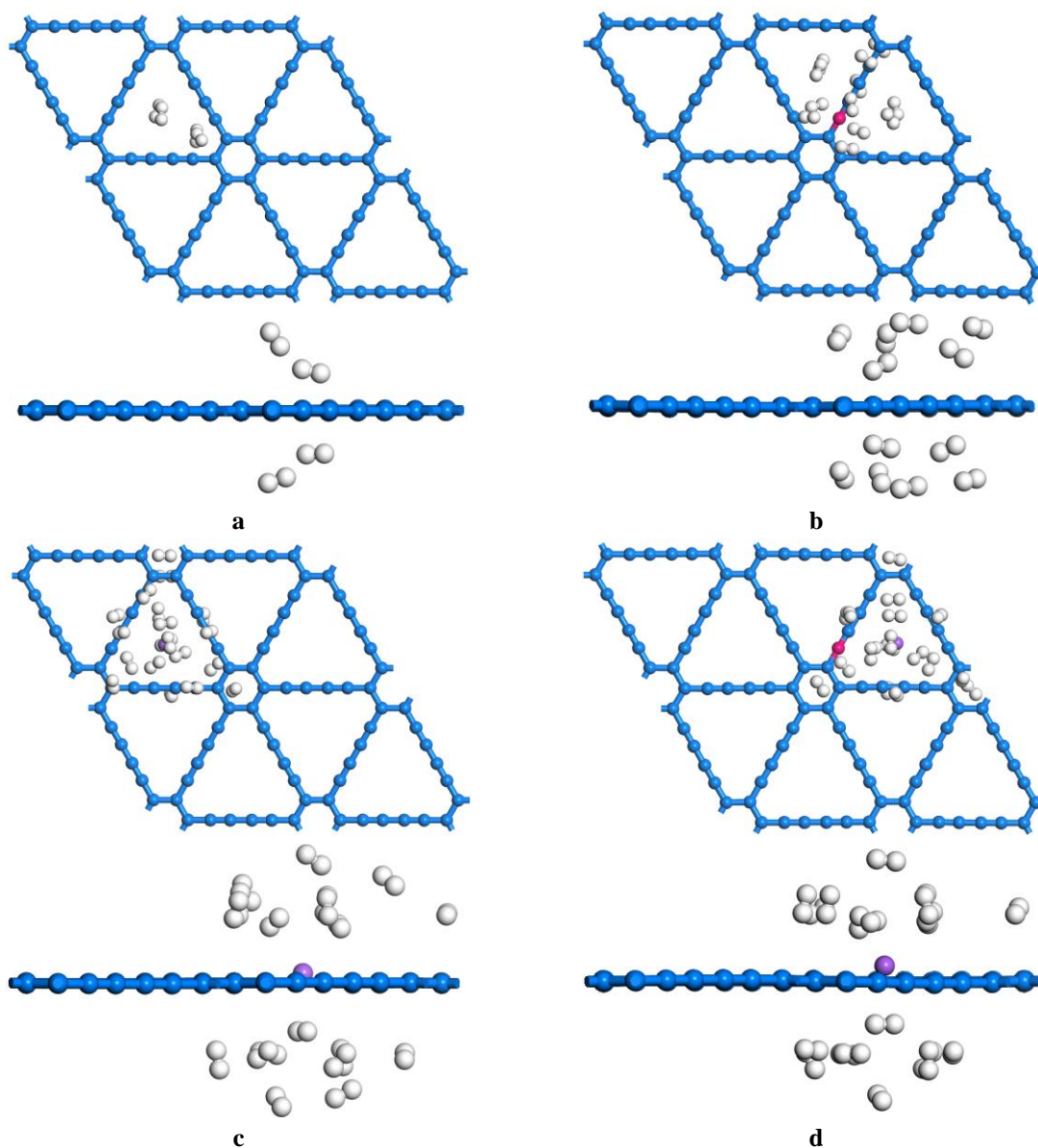
463 4. Conclusion

464 In this study, we thoroughly examined the H_2 adsorption capacity of a carbon structure through
 465 the introduction of specific modifications and a detailed analysis of their effects on the
 466 electrical and structural properties. Specifically, we implemented discrete modifications,
 467 namely N doping and Na decoration, at various locations on the GDY nanosheet. Impurities
 468 introduced into a material can exert a profound influence on its properties, and in the case of
 469 GDY, our study explored the effects of N doping and Na decoration, which introduced three
 470 distinct types of impurities into the structure.

471 By systematically optimizing these modifications, we identified the most favorable positions
 472 for each type of impurity, resulting in GDY structures that combined both decoration and
 473 doping impurities. Our investigations led us to the conclusion that substituting the N atom at
 474 the C2 position with sp hybridization yielded the most stable structure among the N-doped
 475 GDY configurations, with a binding energy of -7.231 eV. The addition of N atoms introduced

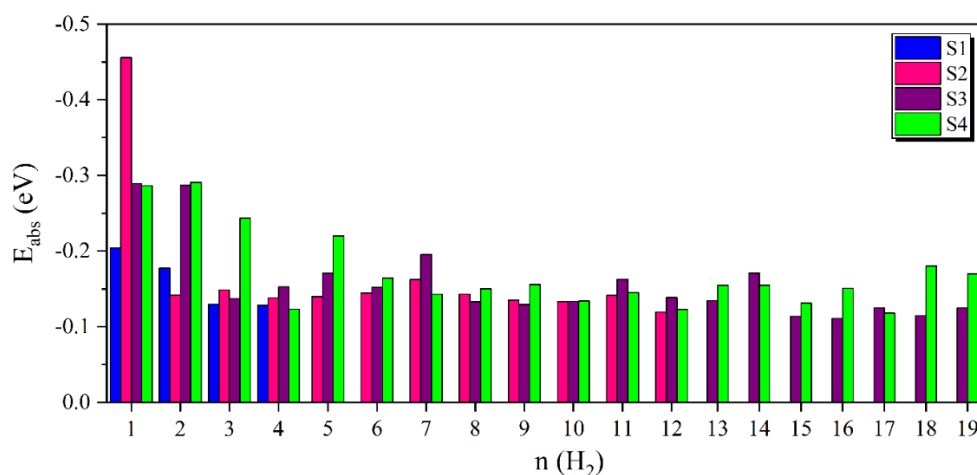
476 structural changes due to the smaller atomic radius of N compared to C and differences in
477 electronegativity between these atoms. These changes influenced bond lengths and
478 transformed the structure from a semiconductor to a semi-metallic material.

479



480 **Fig. 10.** Top and side views of the (a) 4H₂/S1, (b) 12H₂/S2, (C) 19H₂/S3, and (d) 19H₂/S4 structures

481



482

483 **Fig. 11.** The average adsorption energy (E_{ads}) of each step against the number of H_2 molecules adsorbed on S1-
 484 S4 structures.

485

486 Furthermore, the inclusion of Na atoms led to alterations in the charge distribution within the
 487 structure. The partial density of states (PDOS) diagrams revealed an increase in electronic
 488 states above the Fermi level, indicating enhanced conduction in Na-decorated GDY. We also
 489 explored the optimal sites for H_2 adsorption on both pristine and modified GDY structures, and
 490 our results indicated that the modified structures exhibited higher H_2 adsorption energies
 491 compared to the pristine structure. N-doped GDY displayed the highest H_2 adsorption energy,
 492 while the interaction between the H_2 molecule and the carbon atoms in the GDY structure
 493 remained limited, resulting in weaker binding.

494 According to the results, H3 is the best site for adsorption of H_2 on S1, S2, and S3, while M is
 495 the optimal site for H_2 adsorption on S4. The highest adsorption energy value observed was
 496 approximately $40 \text{ kJ}\cdot\text{mol}^{-1}$, indicating that Van der Waals forces primarily drive the adsorption
 497 of H_2 on the nanosheets and is a physical adsorption [47].

498 Additionally, we investigated the maximum H_2 adsorption capacity for each structure by
 499 incrementally adding H_2 molecules. The results of this section show that the H_2 adsorption
 500 capabilities of S3 (Na-doped GDY) and S4 (N, Na-GDY) are almost three times more than S1

501 (pristine GDY). The S1, S2, S3, and S4 structures demonstrated the capacity to adsorb up to 4,
502 12, 19, and 19 H₂ molecules, with average adsorption energies of -0.159, -0.166, -0.156, and -
503 0.170 eV per H₂, respectively. Notably, the Na-decorated GDY structure, S3, exhibited the
504 highest H₂ storage capacity, reaching 13.8 wt%. This theoretical investigation highlights the
505 potential of modified GDY nanosheets for hydrogen storage applications. It also points out
506 promising prospects for improving H₂ adsorption capacity, storage, and detection through
507 modifying the carbon structure.

508

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512

513 **References**

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