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First-principles study of Li-doped planar g-C₃N₅ as reversible H₂ storage material

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Under the background of energy crisis, hydrogen owns the advantage of high combustion and shows considerable environment friendliness; however, to fully utilize this novel resource, the major hurdle lies in its delivery and storage. The development of the in-depth yet systematical methodology for two-dimensional (2D) storage media evaluation still remains to be challenging for computational scientists. In this study, we tried our proposed evaluation protocol on a 2D material, g-C₃N₅, and its hydrogen storage performance was characterized; and with addition of Li atoms, the changes of its electronical and structural properties were detected. First-principles simulations were conducted to verify its thermodynamics stability; and, its hydrogen adsorption capacity was investigated qualitatively. We found that the charges of the added Li atoms were transferred to the adjacent nitrogen atoms from g-C₃N₅, with the formation of chemical interactions. Thus, the isolated metallic sites tend to show considerable electropositivity, and can easily polarize the adsorbed hydrogen molecules, and the electrostatic interactions can be enhanced correspondingly. The maximum storage capacity of each primitive cell can be as high as 20 hydrogen molecules with a gravimetric capacity of 8.65 wt%, which surpasses the 5.5 wt% target set by the U.S. Department of Energy. The average adsorption energy is ranged from -0.22 to -0.13 eV. We conclude that the complex 2D material, Li-decorated g-C₃N₅ (Li@C₃N₅), can serve as a promising media for hydrogen storage. This methodology provided in this study is fundamental yet instructive for future 2D hydrogen storage materials development.

KEYWORDS

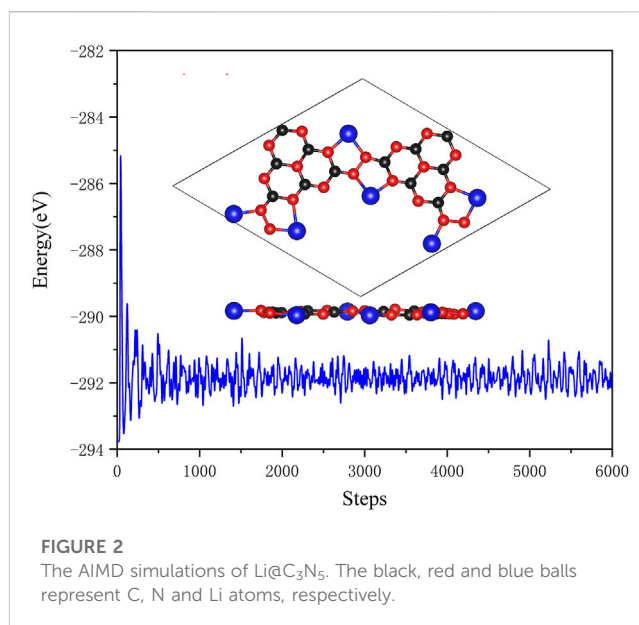
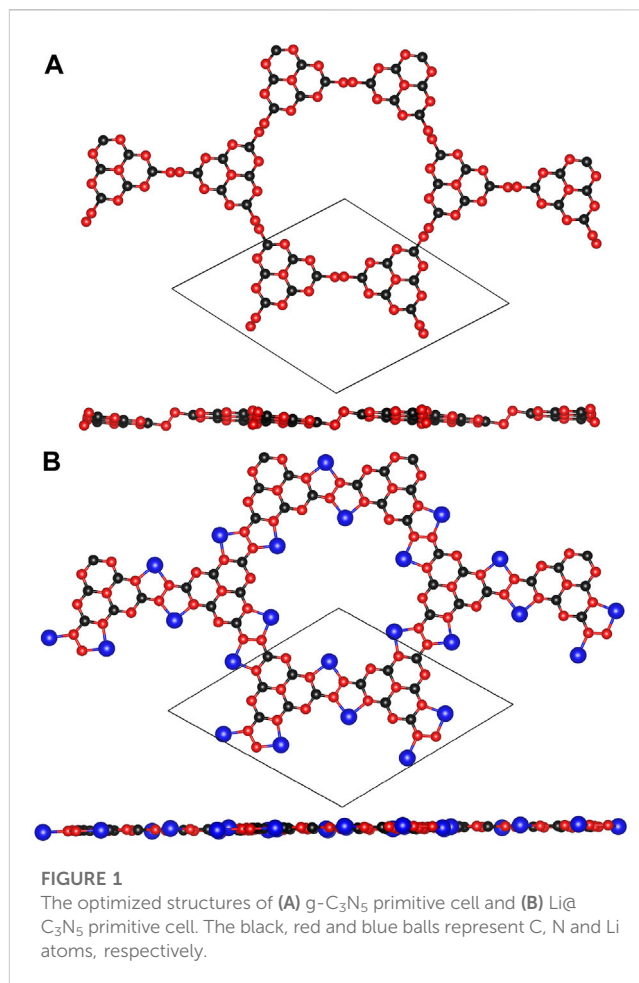
hydrogen storage, reversible, g-C₃N₅, Li-decorated, DFT

1 Introduction

Under the context of global energy crisis, development of clean yet renewable resource is highly needed. Hydrogen, which is regarded as the fuel of future, owns the advantage of high renew-ability, and its combustion has zero-emission of CO₂ (Allendorf et al., 2018; Züttel, 2004; U.S Department of Energy, 2020); thus it can be widely applied in many fields. However, in real practice, the main limitation lies in the fact that we are lack of high-efficiency storage media (U.S Department of Energy, 2020; Huang and Autrey, 2012; Züttel, 2003). Solid state materials based media are preferred due to their superior properties. In the current stage, some researchers tend to use metal-organic frameworks (MOFs) or metal hydrides based materials for this task (Bogdanovi and Schwickardi, 1997; Züttel et al., 2003; Sakintuna et al., 2007; Graetz, 2009; Gao et al., 2022); and at the same time, hydrocarbons or BN compounds had also been reported to own high content of hydrogen (Campbell et al., 2010; Luo et al., 2011a; Luo et al., 2011b; Teichmann et al., 2012; Gao et al., 2020; Gao and Zhang, 2020; Gao and Zhang, 2021). To successfully develop a high-performance hydrogen storage media, not only the storage capacity should be highlighted, manufacturing convenience is also crucial.

Within the past few decades, 2D carbon materials based storage media are promisingly emerging due to their high adsorption ability (Jürgens et al., 2003; Holst and Gillan, 2008; Thomas et al., 2008; Wei and Jacob, 2013; Algara-Siller et al., 2014; Dong et al., 2014; Fina et al., 2015; Hussain et al., 2016; Liu et al., 2019; Wang et al., 2019; Gao et al., 2021a; Wang et al., 2023; Zhang et al., 2023). These kinds of materials own superior aperture structures that enable themselves to be easily doped metal atoms or superalkali clusters for properties optimization and performance enhancement (Zhang et al., 2009; Wu et al., 2013; Zhu et al., 2014; Mahmood et al., 2015; Nair et al., 2015; Ruan et al., 2015; Wei et al., 2016; Gao et al., 2019; Panigrahi et al., 2020; Gao et al., 2021b; Gao et al., 2021c; Chen et al., 2021). Moreover, their original structure features can be qualitatively correlated with their optimizability and functions; thus computational investigation and evaluation of the novel derivatization units can be highly instructive for experimental practice (Wang et al., 2018; Bafekry et al., 2021). The graphene-like 2D unit, g-C₃N₅, is reported to be one of the most promising structures for electronic and optical devices development; and, it is proposed to own higher adsorption carrier, making itself suitable for storage media design.

Moreover, a systematic computation protocol for 2D materials' hydrogen storage performance evaluation is of great importance for future studies; in this study, we proposed a density functional theory (DFT) calculations based methodology for the solution of structural and electronic properties of the pristine and metal-doped 2D materials, and the rules of the correlation between the properties and functions were summarized as reference. We tried our methodology upon Li@C₃N₅; and its hydrogen adsorption mechanism was successfully summarized. We anticipate that the fundamental insights provided in this study will be highly instructive for future development of 2D energy storage media.



2 Computational details

First-principles calculations were carried out within the Vienna Ab-initio Simulation Package (VASP) under periodic boundary conditions (Kresse and Furthmüller, 1996; Grimme, 2006). Considering the

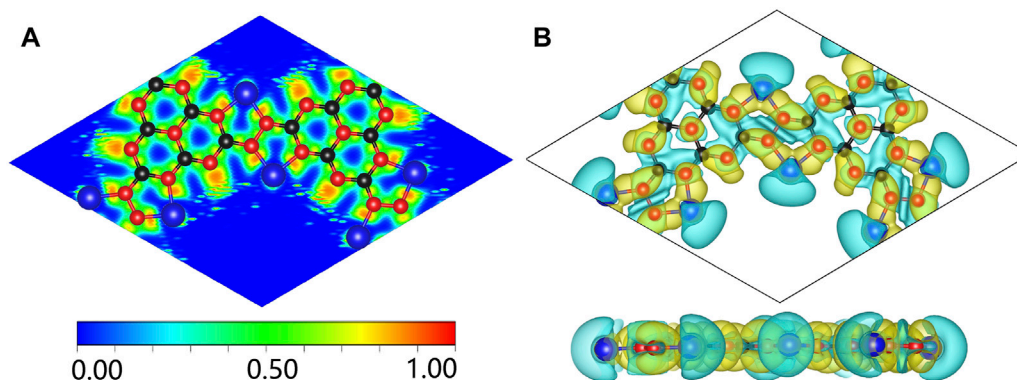


FIGURE 3

(A) The simulated ELF of $\text{Li}@C_3N_5$; the isosurface value is set to be 0.0013. (B) The calculated charge density difference of $\text{Li}@C_3N_5$. The black, red and blue balls represent C, N and Li atoms, respectively.

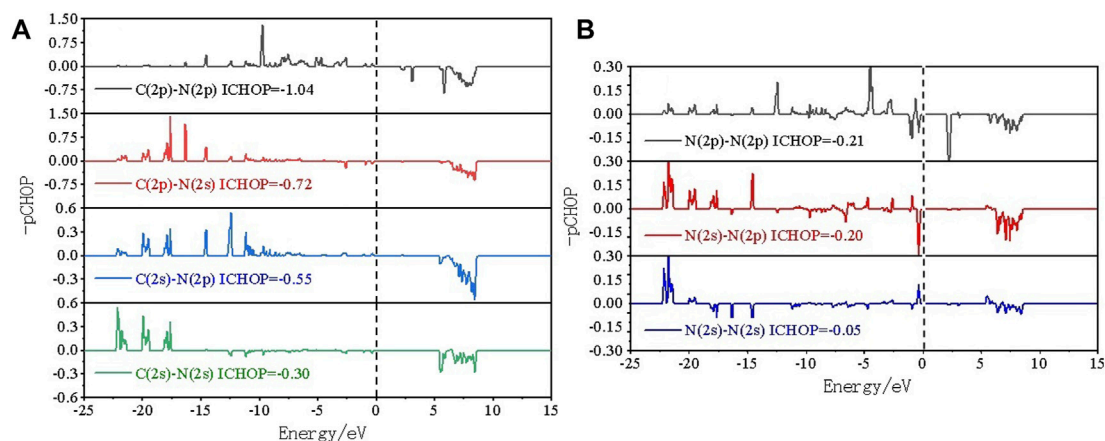


FIGURE 4

Crystal orbital Hamilton population COHP analysis of (A) C-N and (B) N-N bonds within pristine $g\text{-}C_3N_5$.

balance between cost and efficiency, $g\text{-}C_3N_5$ primitive cell was selected as a prototype, and the applied lattice parameters were $a = b = 15 \text{ \AA}$. The electronic states were explored with the plane wave basis projector augmented wave (PAW) method (Blöchl, 1994), the cutoff of energy is set to 520 eV. The exchange-correlation energies were obtained with the generalized gradient approximation, by the PBE method (Perdew–Burke–Ernzerhof) (Perdew and Wang, 1992; Perdew et al., 1996). The convergence of the Hellmann-Feynman forces is 0.01 eV/\AA . The conjugate-gradient algorithm was employed for structural relaxations with an energy convergence criteria of $1 \times 10^{-5} \text{ eV}$. The post-processing of figures were conducted by VESTA. In our calculations, Van der Waals (VDW) corrections are included to describe long-range interactions with the DFT-D2 method (Grimme, 2006). To avoid the interactions between the periodic slabs along the z -axis, the vacuum layer with the magnitude of 20 \AA was inserted. Bader analysis was employed to estimate the amount of charge transferred among the pristine $g\text{-}C_3N_5$ surface and Li atoms (Bader, 1990). And, a $3 \times 3 \times 1$ Gamma-centered k -point grid was used for sampling within the Brillouin zone (Monkhorst and Pack, 1976; Chadi, 1977).

The thermodynamics stability of $\text{Li}@C_3N_5$ was investigated by first-principles molecular dynamics (MD) simulations under the canonical (NVT) ensemble (Martyna et al., 1992). The adsorption energy of Li atom upon $g\text{-}C_3N_5$ were obtained by the equation below:

$$E_{ad}(\text{Li}) = [E(\text{Li}_k \circ C_3N_5) - E(C_3N_5) - kE(\text{Li})]/k, \quad (1)$$

where k represents the number of Li atoms, and E is the energy term. The averaged adsorption energy per hydrogen molecule was calculated by the following equation:

$$E_{ad}(\text{H}_2) = [E(n\text{H}_2 \bullet \text{Li}_k \circ C_3N_5) - E(\text{Li}_k \circ C_3N_5) - nE(\text{H}_2)]/n, \quad (2)$$

where n indicates the number of adsorbed hydrogen molecules upon the surface of $\text{Li}@C_3N_5$. The hydrogen storage capacity can be obtained by the following equation:

$$\text{HSC} = \frac{m(\text{H}) * M(\text{H})}{m(\text{C}) * M(\text{C}) + m(\text{N}) * M(\text{N}) + m(\text{Li}) * M(\text{Li})} \times 100\%, \quad (3)$$

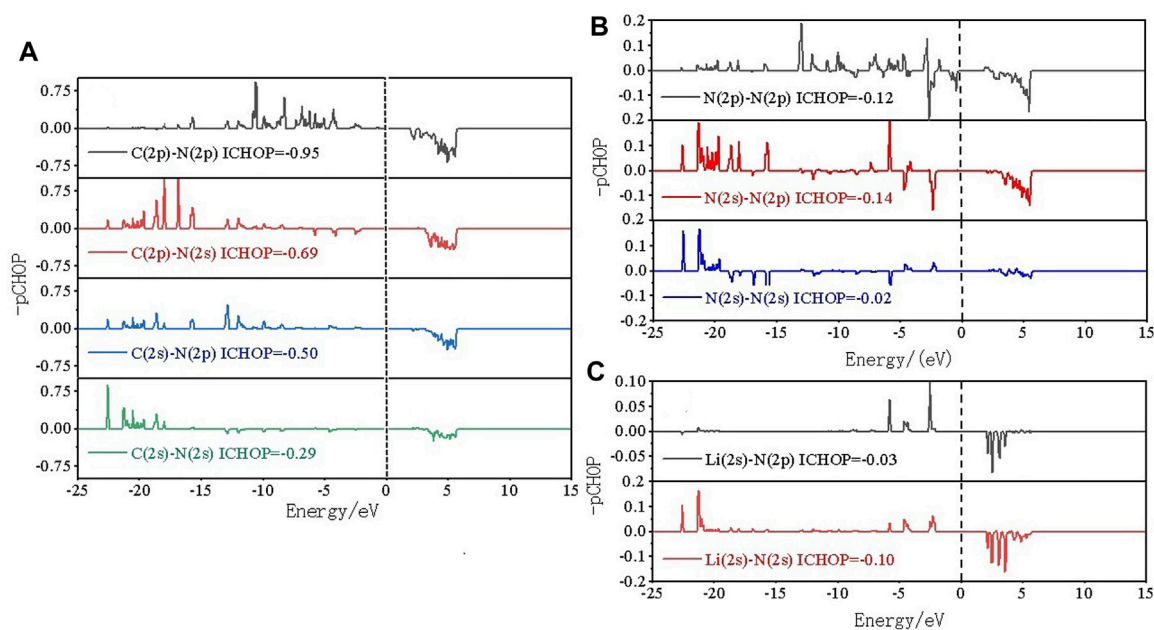


FIGURE 5
COHP analysis of (A) C-N, (B) N-N and (C) Li-N bonds within Li@C₃N₅.

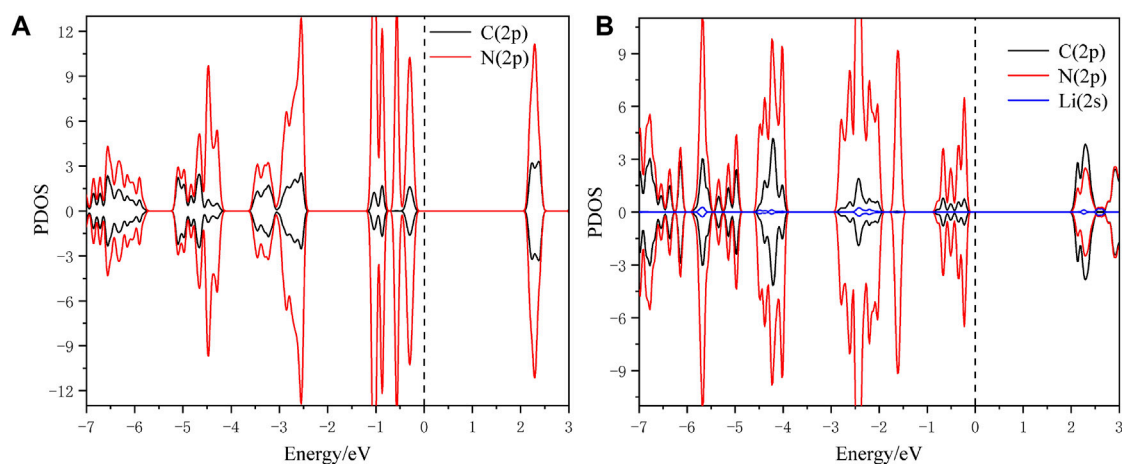


FIGURE 6
The simulated PDOS of (A) pristine g-C₃N₅ and (B) Li@C₃N₅.

where $m(X)$ is the number of X ($X = C, N, Li,$ and H) atom, and $M(X)$ is the corresponding molar mass. The desorption temperature (T_D) between hydrogen molecules and the substrate can be defined as:

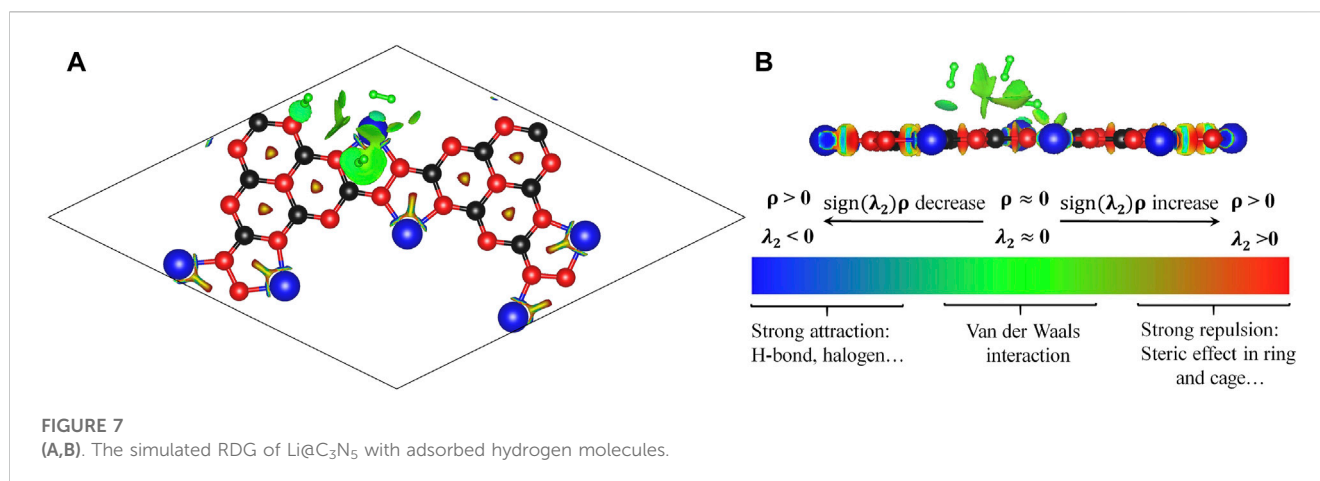
$$T_D = \frac{E_{ad}}{K_B} \left(\frac{\Delta S}{R} - \ln P \right)^{-1}. \quad (4)$$

Here, R and K_B are the universal gas constant and Boltzman constant, respectively; ΔS is the change of entropy for hydrogen molecules from the gas to liquid state ($75.44 \text{ J mol}^{-1} \text{ K}^{-1}$); while P is the pressure of equilibrium (1 atm).

3 Results and discussion

3.1 Structural and electronic properties of Li-doped g-C₃N₅

The optimized configurations of pristine and Li@C₃N₅ were presented in Figure 1. To systematically estimate its thermodynamics stability, *ab initio* molecular dynamics (AIMD) simulations were conducted, and the results were shown in Figure 2 for reference. It is notable that under the temperature of 400 K, the fluctuation of the total energy mainly



oscillates at the equilibrium point; and from the snapshot that reflects the complex structure of the last frame, we noticed that the Li atom can stably bind with the N atom of the g-C₃N₅. All the observations indicate the high stability of this complex 2D material. At the same time, the mechanical properties of the pristine g-C₃N₅ (see in Figure 1A) were also investigated, and the simulated independent elastic constants are: $C_{11} = 17.05$ N/m, $C_{12} = 15.24$ N/m, and $C_{66} = 0.91$ N/m, respectively. These obtained values satisfy the Born-Huang criterion, revealing that the such a CN bonding network displays considerable mechanical hardness.

To in-depth solve the binding mechanism of g-C₃N₅ monolayer, the electronic localization function (ELF) and charge density difference calculations were carried out, the results are presented in Figures 3A, B. The crystal face was obtained by cutting the g-C₃N₅ primitive cell based on the Mille index $(-2.528, 1, 379.194)$. One can clearly see that the calculated ELF value of N-C binding is around 0.8 that is, within the reasonable range of covalent bonds. To further investigate the strength of this kind of binding, the Crystal Orbital Hamilton Population (COHP) calculations were employed, and the calculated results of N-N and N-C bonds are -0.46 and -2.61 eV, respectively (more details can be found in Figures 4A, B). With addition of Li atoms, we noticed that both the N-N (changed to -0.28 eV) and N-C (changed to -2.43 eV) bonds become weaker (more details can be found in Figures 5A–C), further indicating the fact that the charges of Li atoms are effectively transferred to the antibonding orbitals of C-N and N-N bonds. And for pristine g-C₃N₅, we notice the antibonding states move down to the Fermi level, further indicating its capability of adsorbing metallic atoms that own ability of electron donating. The partial density of states (PDOSs) were also calculated for reference, and the results are shown in Figure 6. We can notice that the state density component of conduction band bottom and valence band top were both dominated by the 2p orbitals of N atoms, while less contributions were from 2p orbitals of C atoms.

The N-2p and C-2p orbitals overlap at the energy interval, indicating chemical interactions among these two atoms; such an

observation is consistent with the conclusion obtained by ELF calculations. We hope these theoretical insights could be instructive for future experiment work upon this novel 2D material.

With the addition of Li atoms (the configuration is shown in Figure 1B), we first estimated the absorption energy per metal atom upon this 2D material; the obtained value is around -4.88 eV, within the reasonable range to overcome the risk of cohesive effects. Secondly, we notice that its 2s orbital can effectively overlap with the 2p orbitals of N atoms from g-C₃N₅ within the ranges of $-2.5 \sim -2$ eV and $-4.5 \sim -4$ eV, respectively. (details can be found from the simulated PDOSs shown in Figure 6), indicating the binding availability between these atoms. And also, from the calculated results of ELF, we can confirm that there exist chemical interactions between the added Li atoms and g-C₃N₅ monolayer. With the assistance of Bader analysis, we figure out each Li atom transfers $0.89 e^-$ to g-C₃N₅, and displays electropositivity. Such an observation further indicates the possible potency of these metallic sites for gas molecules adsorption due to enhanced electrostatic interactions.

3.2 Hydrogen storage performance in Li@C₃N₅

Then we optimized the geometric configurations of Li@C₃N₅ with adsorbed hydrogen molecules by first-principles calculations. We can clearly see that the adsorbed hydrogen molecules can be easily polarized by the metallic sites that display considerable electropositivity, consistent with our previous conclusion. We can also see from the calculated reduced density gradient (RDG) shown in Figure 7, the electrostatic interactions between these polarized hydrogen molecules and Li atoms can be correspondingly enhanced. And from the results shown in Figure 7, the main interaction between the adsorbed hydrogen molecules and Li atoms can be attributed to van der Waals interaction.

The optimized configurations of Li@C₃N₅ with multiple adsorbed hydrogen molecules are presented in Figure 8 for reference. The corresponding results are listed in Table 1. The

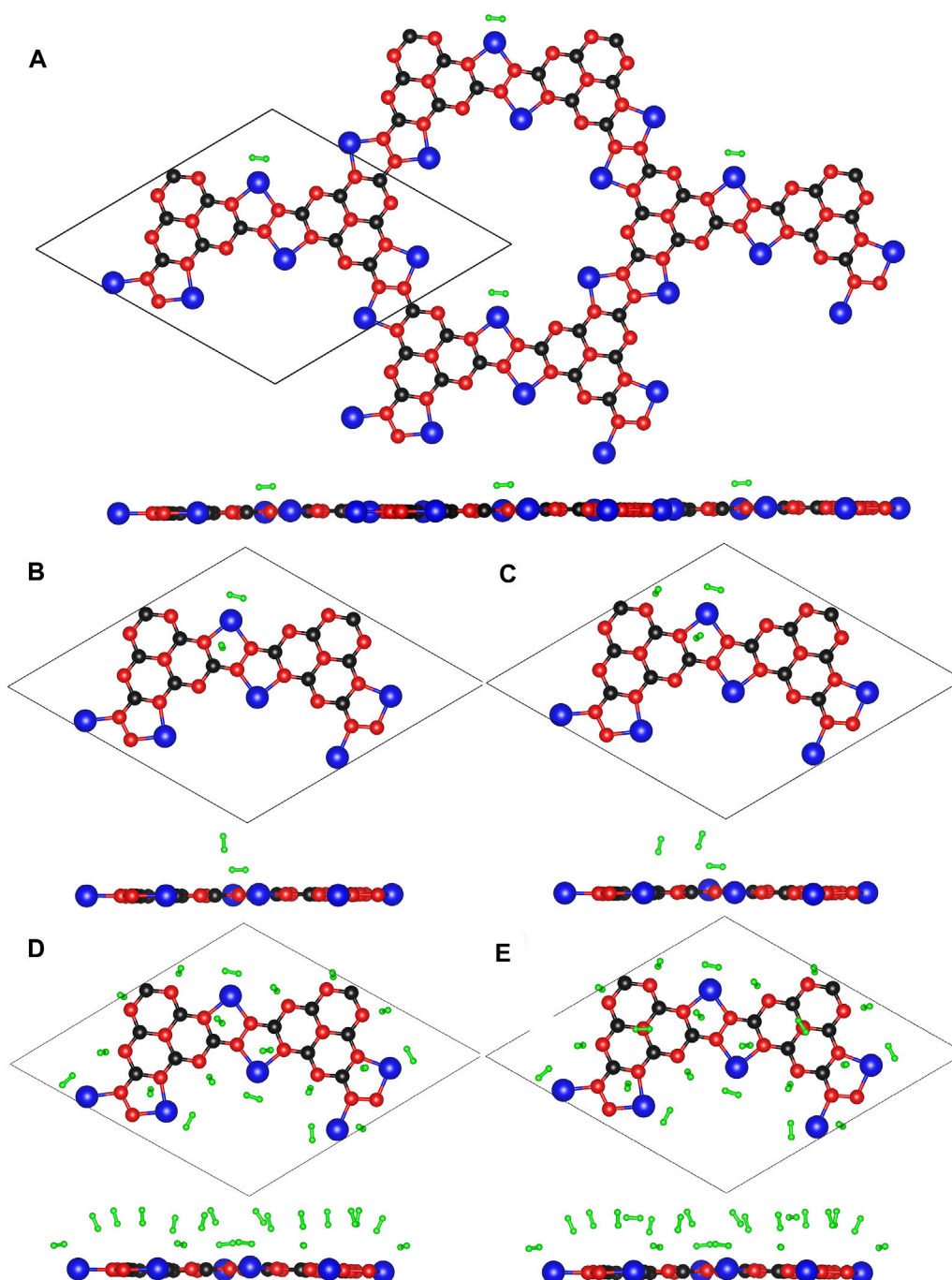


FIGURE 8
(A–E) The optimized configurations of Li@C₃N₅ with multiple adsorbed hydrogen molecules.

averaged adsorption energy per H₂ molecule is ranged from -0.22 to -0.13 eV, with the storage capacity from 0.43 to 8.65 wt%. And for the adsorbed hydrogen molecules, the binding length of H–H is predicted to be slightly stretched between 0.753 Å and 0.755 Å. As stated before, the behind reason can be attributed to the induced polarization by addition of metal atoms. We also

anticipated that the storage capacity can be further increased, with the decoration of extra metal atoms. We conclude that the overall electronic structures of 2D monolayer materials can be favorably improved with respect to specific needs of adsorption tasks in real practice, further indicating a promising methodology by computational evaluation for functional materials design.

TABLE 1 The average adsorption energy E_{ad} , the average bond length R_{H-H} , the desorption temperature T_d and the hydrogen storage density (HSC) for $Li@C_3N_5$ monolayer.

Systems	E_{ad} (eV)	R_{H-H} (Å)	HSC (wt%)	T_d (K)
$Li@C_3N_5-1H_2$	-0.22	0.755	0.43	283
$Li@C_3N_5-2H_2$	-0.15	0.754	0.80	187
$Li@C_3N_5-3H_2$	-0.13	0.754	1.29	167
$Li@C_3N_5-18H_2$	-0.13	0.754	7.79	167
$Li@C_3N_5-20H_2$	-0.13	0.753	8.65	167

4 Conclusion

In summary, we proposed a systematic methodology for 2D materials' hydrogen storage performance evaluation; and we decently investigated the adsorption mechanism of $Li@C_3N_5$ monolayer. DFT computational studies reveal that the pristine $g-C_3N_5$ cannot form strong interactions with hydrogen molecules; by decoration of Li atoms, its structure and electronic properties can be modified. Binding interaction between the added Li atoms and the adjacent N atoms from $g-C_3N_5$ is proved to be stable. Bader charge analysis reveals that each Li atom can transfer $0.89 e^-$ to the pristine $g-C_3N_5$ and display considerable electropositivity. These metallic sites can essentially polarize the adsorbed hydrogen molecules and generate stronger electrostatic interactions, leading to the enhanced hydrogen adsorption performance. The average adsorption energy per hydrogen molecule on the $Li@C_3N_5$ complex 2D material is up to $-0.22 eV$ that is, within a reasonable range; and each primitive cell can adsorb up to 20 hydrogen molecules, and the overall storage capacity can reach to 8.65 wt%. The insights obtained by this study indicated that the $Li@C_3N_5$ can serve as a promising storage media; and moreover, the proposed methodology is highly instructive for future studies.

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Data availability statement

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

Author contributions

XC: Conceptualization, Investigation, Software, Writing–original draft, Writing–review and editing. ZL: Formal Analysis, Writing–original draft. JC: Formal Analysis, Writing–original draft. JL: Formal Analysis, Writing–original draft. DG: Formal Analysis, Writing–original draft. Liang Zhang: Formal Analysis, Writing–original draft. XN: Formal Analysis, Writing–original draft. NW: Data curation, Writing–original draft. GW: Data curation, Writing–original draft. PG: Writing–original draft.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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