Ultrahigh hydrogen storage capacity of holey graphyne

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Abstract
Holey graphyne (HGY), a novel two-dimensional (2D) single-crystalline carbon allotrope, was recently synthesized by Castro–Stephens coupling reaction. The naturally existing uniform periodic holes in the 2D carbon–carbon network demonstrate its promising potential in energy storage. Herein, we conduct density functional theory (DFT) calculation and \textit{ab initio} molecular dynamics simulations (AIMD) to predict the H storage properties of a single-layer HGY sheet modified by Li metal atoms. The DFT calculations demonstrate that Li atoms can bind strongly to the HGY sheet without forming clusters, and each Li atom can anchor four H\textsubscript{2} molecules with an average adsorption energy of about \(−0.22\) eV/H\textsubscript{2}. The largest H storage capacity of the doped HGY sheet can reach as high as 12.8 wt\%, showing that the Li/HGY complex is an ideal H storage material at ambient conditions. In addition, we investigate the polarization mechanism of the storage media and find that the polarization originates from the electric field induced by both the ionic Li atoms and the weak polarized H\textsubscript{2} molecules. Finally, the desorption mechanism of the adsorbed H\textsubscript{2} molecules is thoroughly investigated using a kinetic AIMD method.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction

Recently, the potential exhaustion of fossil fuel has inspired numerous studies on the search for renewable and sustainable energy resources. As an ideal alternative clean energy source, hydrogen energy has many advantages, such as light weight, high abundance and zero production of greenhouse gases from combustion [1]. The biggest challenge in making full use of hydrogen energy is how to store H\textsubscript{2} in an efficient and safe way with a sufficiently high storage density. In general, H can be stored in three forms: cryogenic liquid H, high-pressure gas, and solid-state materials [2]. Among these, solid-state hydrides are considered as one of the most promising ways to fulfill the requirements of onboard applications, since they offer a compact, safe and affordable method of H storage [2, 3]. However, due to low H storage gravimetric capacity (<2 wt\%) and poor hydrogenation/
storage capacity in Ni- and Al-decorated graphene in H storage applications have also been reported and have theoretically been promising materials for H storage. In contrast, the energy range of −0.2 to −0.7 eV/H₂ (intermediate between the strong physisorption and weak chemisorption states) [6, 7]. It is worthy of mention that the DoE target for onboard H storage for light-duty fuel cell vehicles before 2025 is 5.5 wt% and its ultimate target is 6.5 wt% [6, 7].

Benefiting from large surface area and light weight, carbon-based nanomaterials, including fullerene [8, 9], carbon nanotubes (CNTs) [10], nanocones [11, 12] and graphene [13–16] have been suggested to be promising H storage media in recent years. In particular, unlike zero-dimensional fullerenes and one-dimensional CNTs in which H₂ molecules can only bind from the outer sphere, two-dimensional (2D) nanostructures can use both sides to capture H₂ molecules. However, large-scale application of pristine 2D nanomaterials in H storage is still limited due to their weak hydrogenation ability. In order to overcome this disadvantage, the creation of more active adsorption sites on the surfaces of nanomaterials is needed; one approach is ‘decoration’ with metal atoms. In choosing the functional metal atoms, the most common choice is light alkali metals, represented by Li atoms. Recently, a great number of metal-functionalized 2D nanomaterials, e.g. Li-modified graphene [18], MoS₂ [19], black phosphorene [20], holey C₃N [21], transition metal Sc/Ti-decorated C₃N [22], Sc (or Ti/Ni/V)-decorated g-C₃N₄ [23] and Ti-doped ψ-graphene [24] have been predicted theoretically to be promising materials for H storage. In experimental studies, metal-doped 2D carbon nanomaterials in H storage applications have also been reported and have shown promising results so far. Gu et al [25] investigated the H storage capacity in Ni- and Al-decorated graphene nanosheets and found the maximum H storage uptake of the Ni/Al/graphene composites reached up to 5.7 wt%. In another experimental study, Ni-doped graphene like material nanocomposites were found to serve as effective catalysts of hydrogenation–dehydrogenation and possessed a high reversible H capacity exceeding 6.5 wt% [26]. Therefore, functionalized carbon nanomaterials have been demonstrated as promising H storage materials not only from theoretical prediction but also in terms of practical implementation.

Among various 2D materials, graphene (GY) [27], a theorized one-atom-thick C allotrope consisting of sp² hybridized carbons (benzene rings) bridged by ethylenic groups (sp carbons), is expected to possess many unique properties that give it tremendous application potential in the fields of electronics, optoelectronics, catalysis, sensors and energy [28–36]. Over the past few years, many analogous structures of GY, e.g. GDY [37, 38], CEY [39], BGDY [40], and H-, F- and Me-GY [41] have been synthesized successfully, and some of them have demonstrated huge advantages for H storage [30–34]. Most recently, a novel GY material, 2D single-crystalline holey graphyne (HGY), was fabricated by Castro–Stephens coupling reaction from 1,3,5-tribromo-2,4,6-triethylbenzene [42]. The C–C 2D network is alternately connected between benzene rings and sp bonds. The most recent success in synthesis of HGY nanosheets provides an updated account of the scientific and applied interest and prospects in the catalysis, sensor and energy fields. Importantly, due to the naturally existing uniform holes in the geometrical structure of an HGY sheet, it may be a good candidate for energy storage. In this paper, we conduct an ab initio prediction of its potential in H storage. It is found that a pristine HGY sheet without any extra atoms is not suitable to capture H₂ molecules because of its weak adsorption energy, while a Li-decorated HGY can result in a medium- to ultrahigh-capacity H storage of 12.8 wt% with an average adsorption energy of about −0.22 eV/H₂. Our results suggest it is a potential host material for H storage.

2. Computational details

All the first-principles calculations were performed by using density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) [43, 44] with the projector-augmented wave method. The Perdew–Burke–Ernzerhof (PBE) [45] generalized gradient approximation up to 500 eV was chosen as the exchange-correlation functional. A Monkhorst–Pack k-mesh of 5 × 5 × 1 was used to sample the Brillouin zone in the structure optimization for single-layer HGY. The convergence for energy was chosen as 10⁻⁶ eV between two steps. Both the lattice constants and internal coordinates were optimized until the Hellman–Feynman force on each atom was less than 10⁻² eV Å⁻¹. A vacuum space of 20 Å was taken to safely avoid the interactions in the nonperiodic directions. The optimized lattice constants for the HGY monolayer were a = b = 10.85 Å, and a supercell composed of 2 × 2 unit cells was chosen for calculations of H storage on HGY. In our treatment of van der Waals correction, the empirical correction scheme of Grimme (DFT + D2) [46] was employed. To check the structural stability of the system up to high temperatures, ab initio molecular dynamics (AIMD) as implemented in VASP were performed in several cases.

We define the binding energy (Eₖ) of the HGY monolayer with Li atoms using the expression

\[
Eₖ = \frac{1}{n}(E_{HGY+nLi} - E_{HGY} - nE_{Li}),
\]

where \(E_{HGY+nLi}\) and \(E_{HGY}\) are the total energies of the HGY monolayer with and without Li adsorption, respectively. \(E_{Li}\) and \(n\) are the energy of an isolated Li atom and the number of Li atoms, respectively.
The average adsorption energy $E_{\text{ads}}$ of H2 molecules absorbed on Li-decorated HGY are investigated using the relation:

$$E_{\text{ads}} = \frac{1}{m}(E_{\text{HGY} + nLi + mH_2} - E_{\text{HGY} + nLi} - mE_{H_2}),$$

(2)

where $E_{\text{HGY} + nLi + mH_2}$ is the total energy of a Li-decorated HGY sheet with $mH_2$ molecules. $E_{H_2}$ represents the energy of an isolated H2 molecule, and $m$ is the number of H2 molecules.

3. Results and discussion

The geometrical structure of an HGY sheet is shown in figure 1(a). For comparison, we also plotted the structure of GY [27] in figure S1 (available online at stacks.iop.org/NANO/32/215402/mmedia) of the Supporting Information (SI). Single-layer HGY adopts a graphene-like hexagonal lattice structure with space group P6/mmm. In each unit cell of HGY, there is a total of 24 C atoms that can be divided into two different types (C1 and C2; see figure 1), while there are four types of C–C bonds including two $sp^2$–$sp^2$ bonds ($B_1 = 1.463 \text{ Å}$, $B_2 = 1.397 \text{ Å}$), one $sp$–$sp^2$ bond ($B_3 = 1.414 \text{ Å}$) and one $sp$–$sp$ bond ($B_4 = 1.227 \text{ Å}$). An HGY sheet can be considered as hexagonal benzene rings joined together by acetylenic linkages (–C≡C–), which is similar to GY (figure S1). The major difference between GY and HGY is that, in structures of GY, three acetylenic linkages surround to form a large triangular pore, and the angles between acetylenic linkages and benzene rings are about 120°. Moreover, two adjacent acetylenic linkages in HGY concurrently join to the neighboring benzene rings resulting in an eight-vertex ring. Our optimized lattice constants of HGY are $a = b = 10.85 \text{ Å}$, which agrees well with the experimental report [42].

Figure 1. (a) Top and side views of the atomic configuration of a single-layer HGY sheet. The unit cell is indicated by the red dashed lines. C1 and C2 denote the different C atoms; B1, B2, B3, and B4 denote the different types of C–C bonds; and V, H1, H2, and H3 represent different hole sites in HGY. (b) Calculated phonon spectrum of single-layer HGY; here, only the low-frequency part is plotted so as to clearly show the absence of imaginary modes (the whole spectrum is illustrated in figure S2).

The dynamic stability of a single-layer HGY sheet is verified by phonon dispersion calculation, as shown in figure 1(b), and the absence of imaginary modes reflects the dynamic stability of the structure.

The uniformly distributed holes in an HGY sheet, including middle large pores, six-C benzene rings and eight-vertex rings, may indicate great potential in energy storage; herein, we give a prediction of the H storage capacity of an HGY sheet based on DFT calculations. First, the H storage property of a pristine HGY sheet should be evaluated. To find the most stable adsorption site of a single H2 molecule, we considered four different high-symmetry sites, including four hole sites (V, H1, H2 and H3), two top sites (C1-top, C2-top) and four bridge sites (B1, B2, B3 and B4). The calculated absorption energies for the above possible sites are presented in table S1 of the SI and the most energy-favorable configuration is illustrated in figure 2(a). The low-absorption energies (from $-0.06$ to $-0.04 \text{ eV}$) indicate that the H2 molecules are obviously physisorbed in the HGY sheet, suggesting that H2 adsorption on the pristine HGY sheet without any additional element was too weak to ensure efficient H storage.

An important factor in using nanomaterials in H storage is whether they have no chemical interaction with another of the main gas molecules of the atmosphere. To verify this issue, we investigate the chemical stability of HGY under ambient conditions using AIMD simulations. Since we have excluded the possibility of H2 chemically bonding with the HGY monolayer, the other four common molecules (N2, O2, H2O and CO2) in the atmosphere are considered here. Initially, we put 28N2, 8O2, 4H2O and 4CO2 into a $2 \times 2 \times 1$ HGY supercell. Throughout the AIMD simulations of 5 ps in an NPT ensemble with a controlled pressure of 0 bar and temperature of 300 K, although a slight corrugation in the HGY layer is found, there are no new bonds formed between the HGY substrate and the considered gas molecules; see figure 2(b). Therefore, we can judge that monolayer HGY...
possesses great chemical stability under ambient conditions. This gives us evidence to further discuss the possibility of using this nanomaterial in H storage after appropriate modification.

In order to enhance the H2 adsorption ability of the HGY sheet, modification using Li metal atoms is considered. We begin by checking the adsorption behavior of a single Li atom decorated on the HGY sheet. All the possible adsorption sites on the available symmetry positions are investigated, and the corresponding calculated binding energies are presented in table 1. It is found that only the hole sites can capture Li atoms; when a Li atom was initially placed at the C top sites or C–C bridge sites, it would move to the H3-hole sites. The middle large hole (V-site) is also found unable to capture a single Li atom; instead, it moves to the corner of the two neighboring acetylenic linkages and benzene rings, i.e., H1 hole site, with a binding energy of −2.42 eV. The binding energy of H2-sites (the tops of benzene rings) is calculated as −2.22 eV. The most stable sites are H3-hole sites, i.e. the tops of eight-vertex C rings, with the binding energy −2.47 eV; the obtained configuration is illustrated in figure 3(a).

We notice that the binding energy of Li on pristine graphene was previously reported as 2.09 eV [16], so the binding strengths between Li and HGY at the three adsorption sites (H1, H2, and H3-sites) are all larger than that of Li with pristine graphene. As for GY, all the binding energies between Li and HGY are slightly lower than those of Li with GY at hollow sites of acetylenic linkages (3.29 eV) [30]. This is reasonable because in Li-decorated GY structures, Li atoms bind with three acetylenic linkages, while in a Li-decorated HGY system, there are two acetylenic linkages connected to the Li atoms, which lead to more charge transfer and stronger hybridization between Li and the substrates. Otherwise, another typical carbon nanomaterial, graphdiyne, is reported to have a similar binding energy (−2.35 eV for one Li atom decorated at the core site of two adjacent acetylenic linkages) [32] to the present HGY structure.

Considering the fact that an important issue for H storage in a metal-doped carbon nanomaterial is the avoidance of metal–metal clustering, we investigate the diffusion behaviors of Li ions over and through an HGY monolayer using the climbing-image nudged elastic band method to compute the barriers for movement of a Li atom from one most energy-favorable site (H3-hole site) to another one. Here, three pathways, including the in-plane diffusion paths P1 and P2 and out-of-plane diffusion paths P3, are considered. Among them, P1 denotes the path through which Li migrates from one H3-hole site to the adjacent benzene ring site (H1) and then arrives at another H3-site, P2 is the path through which Li migrates from one H3-hole site to the core of two acetylenic linkages (H2) and then arrives at another H3-site, and the out-of-plane diffusion path P3 is the path passing through the eight-vertex ring from one side to another; see figures 3(b), (d). Our obtained diffusion barriers of Li ions over and through an HGY monolayer are shown in figures 3(c)–(d). The diffusion barriers are calculated as 0.44 eV and 0.26 eV for in-plane paths P1 and P2, and 2.80 eV for the out-of-plane path P3. Obviously, the out-of-plane diffusion barrier is much higher than that of in-plane paths, owing to the small pore size of the eight-vertex ring which results in a larger repulsive Coulomb

Table 1. Calculated binding energies (eV) of single Li atoms decorated on an HGY sheet.

| System Sites | Top C1 | C2 | Bridge B1 | B2 | B3 | B4 | Hole V | H1 | H2 | H3 |
|--------------|-------|----|-----------|----|----|----|-------|----|----|----|
| Binding energy | moved to H3-site | moved to H3-site | moved to H3-site | −2.41 | −2.22 | −2.47 |

Figure 2. (a) Top and side views of the most stable optimized geometry of one H2 molecule absorbed on a pristine HGY. (b) Top and side views of snapshots taken from AIMD simulations of HGY in the atmosphere, where the molecular numbers are chosen as 28N2, 8O2, 4H2O and 4CO2 in a 2 × 2 × 1 HGY supercell. C, O, N and H atoms are represented by brown, red, grey and pink spheres, respectively.
interaction and significantly enhances the diffusion barrier. To prevent metal–metal clustering, the energy barriers should be notably larger than the thermal energy of a Li atom at the highest desorption temperature. Here, we choose a sufficiently high temperature of 450 K (in the following section, one can see that this temperature is higher than the highest desorption temperature). The thermal energy gained by Li atoms can be evaluated by equation (3) based on the equipartition theorem,

$$E_{\text{avg}} = \frac{3}{2} k_B T,$$

where $k_B$ and $T$ are the Boltzmann constant and temperature, respectively. Note that equation (3) is for molecules in three-dimensional space; here, Li atoms vibrate in the plane, so it turns out to be $E_{\text{avg}} = k_B T$. Therefore, the obtained thermal vibration energy at 450 K is only 0.038 eV, which is very small compared to the diffusion barriers, so the movement of Li atoms is restricted. Therefore, we are confident that in this novel carbon nanomaterial Li atoms would be uniformly dispersed without clustering.

In order to further confirm the stability of the system up to high temperatures, we also perform an AIMD simulation. The $NVT$ ensemble is chosen to be the dynamic ensemble with a massive Nosé–Hoover thermostat at a temperature of 300 K. The total simulation time is 5.0 ps, with a time step of 1 fs. After 5000 steps of dynamic simulation, the Li atoms are still decorated around the initial adsorption sites and only a slight corrugation in the HGY layer and some slight movement of Li atoms are found, as illustrated in figure S3. The result indicates that this storage media is thermally stable enough and gives confidence towards the feasibility of practical application of this material in H storage systems.

We then continue to increase addition of Li adatoms onto the HGY sheet. For two Li atoms absorbed in the HGY monolayer, we carefully check the six most energy-favorable configurations, including two Li atoms adsorbed on the opposite sides of the HGY layer at the same $H_1, H_2,$ or $H_3$-sites (figures S4(a)–(c)) and two Li atoms placed on two adjacent $H_1, H_2,$ or $H_3$-sites (figures S4(d)–(f)). The corresponding binding energies are illustrated in table S2. The most energy-favorable configuration of two Li atoms decorated on the HGY is illustrated in figure 4(a), where two Li atoms were adsorbed at two adjacent $H_3$-sites on both sides of the HGY layer. The binding energy of this situation ($-2.46$ eV/Li) is almost identical to that of a single Li atom adsorbed on an $H_3$-site ($-2.47$ eV/Li). Therefore, it is clear that with an increasing number of Li atoms, it is more preferable for the Li atoms to be located on the $H_3$-sites.

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Figure 3. (a) Most energy-favorable configuration of single Li atoms decorated on HGY. (b) Schematics of the in-plane diffusion paths $P_1$ and $P_2$. The diffusion barrier profiles of (c) in-plane diffusion ($P_1, P_2$) and (d) out-plane diffusion ($P_3$).
On the basis of the former analysis, we continually increase the numbers of decorated Li atoms. It is found that at most six Li atoms can be captured in a unit cell of HGY, with three Li atoms located above the sheet and another three below the sheet, as illustrated in figure 4(b). All the Li atoms are located on the tops of the eight-vertex C rings with distances from the HGY sheet of about 1.52 Å. The average binding energy of one Li atom is calculated as \(-2.04\) eV.

Through Bader charge analysis, we find that each Li atom donates about 0.85 \(|e|\) to the C substrate. This charge redistribution induces Coulomb interactions between the Li atoms and HGY sheet, which is not only beneficial to the stability of the 6Li-decorated HGY layer (6Li-HGY) but also may result in a local electric field. In figure S5, we present the charge density difference of 6Li-HGY. It is observed that the electrons are depleted around the Li adatoms and accumulate near the C atoms, which leads to a strong electrostatic interaction between the metal atom and HGY. The result is consistent with the above Bader charge analysis.

AIMD dynamics simulations are performed to investigate the thermal stability of 6Li-decorated HGY at 300 K up to 5 ps; the final results are shown in figure S6. One can see that the Li atoms are well stabilized on the HGY layer and without clustering of Li atoms; only a slight corrugation in the HGY layer was found. The result indicates that this storage medium is thermally stable enough and may maintain a good recycle stability.

Now, we turn to discuss the H adsorption on the 6Li-HGY sheet. We start with a single H$_2$ molecule per Li atom absorbed on this storage medium (6H$_2$ in 6Li-HGY). The most favorable adsorption geometry for this case is shown in figure 5(a); the H$_2$ molecules are found to preferentially stick aslant to the Li atoms and tilt slightly toward one of the acetylenic linkages in the HGY sheet. Then, we gradually increase the number of adsorbed H$_2$ molecules on the Li-decorated HGY layer. The most favorable adsorption geometry for two H$_2$ molecules per Li case (12H$_2$ in 6Li-HGY) is shown in figure 5(b). Two H$_2$ molecules are symmetrically distributed on both sides of the Li atom and tilt slightly toward the two adjacent acetylenic linkages of one eight-vertex ring. This symmetrical distribution of H$_2$ molecules is more obvious in three H$_2$ molecules per Li case (18H$_2$ in 6Li-HGY), where three H$_2$ molecules form a nearly regular triangle; see figure 5(c). This tendency mainly stems from the threefold rotational symmetrical potential well induced by the HGY sheet. We find that a maximum of four H$_2$ molecules per Li atom can be adsorbed on the 6Li-HGY layer, as shown in figure 5(d). However, the last H$_2$ molecule has a weak...
interaction with the Li/HGY complex (about −0.08 eV/H2); more importantly, the distance of the fourth H2 molecules from the Li atom is much further than those of the former three H2 molecules, as can be seen from figure 4(d). No more H2 molecules can be captured to the storage medium according to our calculations. Therefore, a maximum of 24 H2 molecules can be captured on both sides of the 6Li-HGY layer, which gives a maximum weight percentage of 12.8 wt%, a value that can significantly surpass the target of the DoE [6, 7]. Compared to other typical GY-like nanomaterials, the maximum H capacity of the present 6Li-HGY sheet is very close to that of Li-modified GY (13 wt% [30]), and much higher than the values obtained in Li-decorated graphynyde (8.81 wt% [32]) and CEY (9.96 wt% [18]) systems.

Table 2 lists the calculated H2 adsorption details, including the average adsorption, the distances of H2 molecules from Li atoms and the H–H bond lengths depending on the number of adsorbed H2 in 6Li-HGY. It can be clearly seen that the average H2 adsorption energy decreases with increasing H weight percentage. For instance, at low gravimetric density (6H2 in 6Li-HGY), the average adsorption energy for one H2 molecule is 0.31 eV/H2. With an increase in the number of H2 molecules per Li atom, the adsorption energy decreases and is reduced to 0.22 eV/H2 at the maximum gravimetric density (24H2 in 6Li-HGY). Note that all the average adsorption energies fall in the range of −0.2 to −0.7 eV [6, 7], implying the Li/HGY complex is perfect for reversible H2 adsorption/desorption near room temperature.

The projected density of states (PDOS) of 6Li-HGY before and after H2 adsorption are shown in figures 6(a)–(j). A small change in the PDOS of C is found before and after the H2 adsorption, which indicates that a rather weak interaction exists between the H2 molecules and the host materials, i.e. the acetylenic linkages of the HGY sheet. While significant variation in the PDOS of Li after H2 adsorption can be seen, it is obvious that the H2 molecules mainly interact with the Li atoms.

As previously described, there are two types of H2 molecules in the largest H storage situation. The first three connected H2 molecules (first type of H2 molecules) remain close to the Li atoms with an average Li–H distance of about 2.00 Å, while the fourth H2 molecules (second type of H2 molecules) are found relatively far from the Li atoms with an average Li–H distance of about 3.77 Å, but still at the same height as the other three H2 molecules, as illustrated in figure 4(d).

In figure 7, we analyze the charge density difference of 24H2 molecules adsorbed on the 6Li-HGY sheet, which helps us to reveal whether the interaction between the H2 and the substrate sheet is a polarization mechanism or the weak van der Waals force. All the H2 molecules are found to show charge depletion and accumulation, so it is clear that both types of H2 molecules bind with the substrate via the polarization mechanism. As mentioned earlier, both the HGY layer and Li ions are partially charged and this produces a polarized electrostatic field, so the polarization of the first type of H2 molecules is reasonable. For the second type of H2 molecules, the charge redistribution is obviously weaker than that of the first type of H2 molecules as shown in figure 6, but what is certain is that they are also polarized. Considering the fact that the electric field of the ionic Li is almost screened by their own polarized charges caused by the first type of H2 molecules, we can judge that the rather weak polarization of the second type of H2 molecules is induced by the electric field provided by not the ionic Li atoms but the polarized first type of H2 molecules.

To explain this polarization effect in depth, we further perform Bader charge analysis of the system. All the H2 molecules are adsorbed in tilted shape so that one H atom comes close to the Li atom while the second H atom is relatively far from the Li atom. It is found that small amount of charge (−0.08 e) is transferred from Li to the nearest H atoms of the first type of H2 molecule, and an even smaller amount of charge (−0.05 e) is transferred from Li to the nearest H atoms of the second type of H2 molecule. Furthermore, the different polarization effects can also be reflected in the H–H bond lengths of the two types of H2 molecules; the bond lengths in the first type of H2 molecules are obviously elongated and in the range of 0.758–0.764 Å, which is slightly larger than the 0.750 Å of free H2. In contrast, the H–H lengths in the second type of H2 molecules are only slightly elongated (0.752–0.753 Å), implying the much weaker polarization compared to the first type of H2 molecules.

As an ideal recycling H storage medium, the desorption temperature is also a vital parameter. We calculate the desorption temperatures (Td) of each H2 molecule employing the Van ’t Hoff equation [47] as given in equation (4),

$$T_d = \frac{E_b}{k_B} (\Delta S / R - \ln P)^{-1},$$

where Td is the desorption temperature, Eb is the van der Waals corrected H2 adsorption energy (1/H2), kB indicates the Boltzmann constant, R is the gas constant and ΔS represents the change of H2 entropy from gas to liquid phase. P is the pressure (taken here as ambient pressure). The obtained desorption temperatures for different H2 molecules in the 6Li-HGY system are illustrated in table 2; all of them are distributed near room temperature and are ideal desorption temperatures for fuel cell devices.

To further check the desorption temperature evaluations from the Van ’t Hoff equation, we then perform AIMD calculations for hydrogenated 6Li-HGY. Since our obtained
decoration temperatures are in the range of 280–400 K, in the AIMD simulation, four temperatures, 250 K, 350 K, 400 K and 450 K, are mainly examined. The MD simulations employ a supercell containing totally 312 atoms with a time step of 5 ps. Snapshots of MD simulations are displayed in figures 8(a)–(d). It can be seen from figure 8(a), after the production run at 250 K, that about 1/4 to 1/3 H$_2$ molecules can be seen as escaped from the metal atoms; here we take the approximate distance of 0–4 Å between Li–H atoms as an effectual distance. At the simulation temperature of 350 K, more than 1/2 H$_2$ molecules move from Li atoms and start to spread over the supercell (figure 8(b)), and at 400 K, nearly 3/4 H$_2$ molecules escape from the 6Li-HGY complex. Under heating at 450 K for 5 ps, almost 4/5 H$_2$ molecules escape. Generally, our AIMD results are basically accordant with the desorption temperature estimations calculated by the Van ’t Hoff equation. Therefore, our proposed Li-decorated HGY system can serve as a promising reversible H storage candidate.

4. Conclusions

In conclusion, using first-principles calculations, we investigated the H storage behavior of Li-decorated HGY. The numerical results show that such complexes can possess a H storage capacity as high as 12.8 wt%; this gravimetric density is significantly higher than the value obtained in many typical alkali-metal-decorated GY nanomaterials (e.g. CEY, graphdiyne). Meanwhile, the adsorption energy per H$_2$ molecule was −0.22 eV, perfect for reversible H$_2$ adsorption/desorption near room temperature. It was revealed that the polarization mechanisms, which stem from both the electric field induced by the ionic Li decorated on the HGY and the weak polarized H$_2$ molecules, play a key role in the adsorption of H$_2$ molecules. Finally, the desorption mechanisms of the adsorbed H$_2$ molecules were thoroughly investigated using the Van ’t Hoff equation and kinetic AIMD method; the obtained desorption temperatures were found to be near room temperature and are ideal desorption temperatures for fuel cell devices. Our calculations suggest that the newly synthesized Li-atom-decorated HGY is a promising material as a high-capacity H storage medium.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Figure 8. Snapshots (side views) at the end of 5 ps AIMD simulations for the hydrogenated Li-HGY structure at (a) 300 K, (b) 350 K, (c) 400 K and (d) 450 K. The H₂ molecules outside the red dashed boxes can be considered as desorbed from the Li-HGY sheet.
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