Adsorption and Desorption of Tritium on/from Nuclear Graphite

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ABSTRACT: The interaction between graphene-based materials and hydrogen isotopes is of great importance with respect to the adsorption of hydrogen in graphene and the removal of tritium from irradiated nuclear graphite. In the present study, based on density functional theory, we investigate and discuss the adsorption and molecular desorption of hydrogen isotopes on the edges and stable interior defects. The adsorption energy of one hydrogen on graphene-based materials is between $-2.0$ and $-5.0$ eV, which is related to the structure and hydrogenation level. The hydrogenation level increases with the hydrogen partial pressure and decreases with the temperature. The best adsorption pathways of hydrogen isotopes in graphene-based materials are determined, together with three different desorption stages with different activation energies. The desorption peaks of thermal desorption spectrometry agree well with stage 2 and stage 3 of simulation. Our results can provide a theoretical basis for the study of the hydrogen isotope behaviors in graphene and the decontamination of nuclear graphite.

1. INTRODUCTION

As the concern for the environment grows, hydrogen attracts more and more attention as an environmentally friendly energy source. However, one of the biggest problems for hydrogen usage is the storage of hydrogen. Recently, graphene and graphene-based materials have been intensively studied due to their outstanding hydrogen storage capacity. In order to fully master the hydrogen storage technique in graphene-based materials, the interaction between hydrogen and the graphene structure must be investigated. In spite of the need raised by hydrogen storage, the knowledge of the adsorption and desorption behavior of hydrogen isotopes in graphene is also required when dealing with irradiated nuclear graphite. Nuclear graphite has been widely used in various reactors, and there are over 250,000 tons of irradiated nuclear graphite awaiting processing. Despite the accumulation of irradiated nuclear graphite resulting from the operation of existing or decommissioned reactors, graphite will also be used in generation IV nuclear reactors. In irradiated nuclear graphite, tritium is the radionuclide with the highest content and contributes most of the radioactivity in the first few years. In addition, tritium is easily released from irradiated nuclear graphite and eventually causes radiological health problems. Tritium, as an isotope to hydrogen, can be easily transported through the whole graphite structure once the C–H bond resulting from adsorption is broken. Therefore, with respect to the desorption of tritium from nuclear graphite, the determinant step would be the bond breaking of the C–H bond. In irradiated nuclear graphite, the tritium atom was produced from the nuclear reaction of $^6\text{Li}$, $^3\text{He}$, and $^2\text{H}$, and the resultant tritium atom could be easily adsorbed on the adsorption sites in graphite. Through the simulation of hydrogen-isotope atom desorption from the graphene structure, useful information can be provided to the setting of the process of tritium removal from nuclear graphite. Hence, the interaction between hydrogen isotopes and graphite or graphene-based materials is worth a thorough investigation.

Nuclear graphite has been widely used in various reactors, and there are over 250,000 tons of irradiated nuclear graphite awaiting processing. Despite the accumulation of irradiated nuclear graphite resulting from the operation of existing or decommissioned reactors, graphite will also be used in generation IV nuclear reactors. In irradiated nuclear graphite, tritium is the radionuclide with the highest content and contributes most of the radioactivity in the first few years. In addition, tritium is easily released from irradiated nuclear graphite and eventually causes radiological health problems. Tritium, as an isotope to hydrogen, can be easily transported through the whole graphite structure once the C–H bond resulting from adsorption is broken. Therefore, with respect to the desorption of tritium from nuclear graphite, the determinant step would be the bond breaking of the C–H bond. In irradiated nuclear graphite, the tritium atom was produced from the nuclear reaction of $^6\text{Li}$, $^3\text{He}$, and $^2\text{H}$, and the resultant tritium atom could be easily adsorbed on the adsorption sites in graphite. Through the simulation of hydrogen-isotope atom desorption from the graphene structure, useful information can be provided to the setting of the process of tritium removal from nuclear graphite. Hence, the interaction between hydrogen isotopes and graphite or graphene-based materials is worth a thorough investigation.

Received: September 28, 2021
Accepted: December 9, 2021
Published: December 23, 2021
Our previous study\textsuperscript{15} had paid attention to the adsorption and desorption behaviors of the graphite edges absorbing eight hydrogens. We showed the best adsorption pathways of hydrogen on graphite edges and determined the stability of hydrogen-terminated edges and their desorption activation energies. However, there is still a potential adsorption site within the graphite crystallite: in between two adjacent carbon layers, on the basal plane, especially when there are defects. Besides, a graphite edge adsorbing four H atoms is also comparatively favored, which may play an important role when matching the results of simulation with those of the experiment. In this paper, the graphite edge absorbing four H atoms and internal defects was studied based on the density functional theory (DFT) to comprehensively understand the adsorption and desorption behavior of hydrogen isotopes in graphite or graphene-based materials. Considering the negligible van der Waals interaction between two adjacent graphite layers and similar properties between hydrogen and tritium, when studying the interaction between hydrogen isotopes and graphene-based materials, the behavior of hydrogen on one layer of graphene was simulated in our study. Moreover, the desorption experiment on a Chinese nuclear graphite was carried out in the present study through the analysis of the thermal desorption spectrum, and the activation energy of desorption was calculated so that the activation energy calculated from the simulation can be examined.

2. RESULTS AND DISCUSSION

2.1. Structures. The models of the graphite edges and interior defects are shown in Figure 1. The numbers and letters represent different hydrogen adsorption sites. The structures of edges have been shown in our previous study.\textsuperscript{15} Single-vacancy (SV) and double-vacancy (DV) defects are constructed by extracting one and two carbon atoms from the (001) surface. DV defects include DVS-8-5, DVSSS-777, and DVSSSS-6-7777.\textsuperscript{16} Obviously, there are strong and expensive dangling bonds in SV defects, zigzag (ZZ) and armchair (AC) edges, which are distinctly different from other structures. The formation energies of interior defects are given in Table 1. Accordingly, the formation energy of SV defects (7.87 eV) is comparatively high due to the expensive hybridization resulting from the strong dangling bonds, similar to the situation we found when we were studying the formation energy of the ZZ edge (1.22 eV/Å) in our previous research.\textsuperscript{16}

2.2. Adsorption. As shown in Figure 1, the carbon atoms on the SV defects and all edges are sp$^2$-hybridized, and each carbon atom still has two unpaired electrons; thus, adsorption up to two hydrogen atoms occurs on each carbon atom. The carbon atoms on the other structures are sp$^3$-hybridized, and each carbon atom can absorb up to one hydrogen atom. In the present study, we calculated all energetically favorable H-atom adsorption sites on the graphite interior defects. When a H atom is adsorbed on graphite, we only consider the most stable site for each system according to $E_{\text{ad}}$, for example, the most stable adsorption site for one H atom on the DVS-8-5 defect is site 1a, which is marked * at the upper-right corner of $E_{\text{ad}}$. The most stable adsorption site and $E_{\text{ad}}$ for one H atom on the interior defects are shown in Table 2 [\textsuperscript{15,16,17}]. The results agree with the literature values, whose $E_{\text{ad}}$ ranges from −4.35 to −2.14 eV.\textsuperscript{15,16,17} Since the adsorption energy at the

![Figure 1. Geometries of graphite edges and interior defects: (a) AC, (b) ACR, (c) ZZ, (d) ZZR, (e) SW defect, (f) SV defect, (g) defect (DVS-8-5), (h) DV defect (DVSSS-7777), and (i) DV (DVSSSS-6-7777). The numbers and letters represent different hydrogen adsorption sites. The green dashed lines in the interior defects indicate structural symmetry, and the green letters represent different symmetric zones.](https://doi.org/10.1021/acsomega.1c05395)

| interior defects | formation energy (eV) |
|------------------|-----------------------|
| SW               | 5.29                  |
| SV               | 7.87                  |
| DVS-8-5          | 7.60                  |
| DVSSS-777        | 6.34                  |
| DVSSSS-6-7777    | 7.34                  |

SV defect is the lowest, it is the most energetically favored for the first adatom to be adsorbed at the SV defect. The adsorptions for others are weak that stem from the dangling bonds.

The density of states (DOS) describes the distribution and occupancy of the electron orbits of hydrogen and carbon, showing the strength of the bonds between atoms. The crystal orbital Hamiltonian populations (COHPs) partition the band-structure energy into orbital–pair interactions. Like integrating the electronic DOS gives the number of electrons in the system, an energy integral of the COHP shows the contribution of a specific contact (bond) to the band energy: in other words, the integrated COHP hints toward the bond strength, and it comes in electron volts or kilojoules per mole. The charge density describes the spatial distribution of the charges around the atoms, while the charge density difference (CDD) describes the change before and after the bonded atoms, the binding between the atoms, and the electron increase and decrease. The DOS and COHP are plotted in Figure 2, and the CDD of hydrogen adsorption is shown in
Figure 3. With reference to Figure 2, the DOSs of C p states and H s states have high dispersion, and this concept intuitively shows us the strength of the action between C and H atoms. The C−H bond of the SV defect has the highest COHP integral, being 6.47, and the COHP integrals of SW, DV5-8-5, DV555-777, and DV5555-6-7777 defects are 6.16, 6.24, 6.22, and 6.17, respectively. The C−H bond of the SV defect is thus stronger than the others. The CDD in Figure 3 shows that the H atoms interact with the graphite by transferring the electrons.

Our previous study showed that the adsorption of H atoms on the ZZ edge is a highly local process, which is different from the interior defects of this study. The adsorption energies for each adsorbed hydrogen atom at all possible sites at interior defects were calculated, and the most energetically favored adsorption is shown in Table 3. $E_{ad}$ is the adsorption energy of each system of the best adsorption pathways. At SV defects, there are three carbon atoms with six unpaired electrons, as shown in Figure 1 (two unpaired electrons for each carbon atom); therefore, there are six hydrogen atoms altogether that can be adsorbed at one SV defect, while for SW and DV defects, the relaxation of the structure eliminates one induced unpaired electron at each carbon atom near the defect; hence, the number of hydrogen atoms that can be

Table 2. Adsorption Energies ($E_{ad}$) of the First H Atom on the Adsorption Sites (See Figure 1 to Identify the Positions)\(^\text{a}\)

| interior defect | adsorption site | $E_{ad}$ (eV) | interior defect | adsorption site | $E_{ad}$ (eV) |
|-----------------|----------------|--------------|----------------|----------------|--------------|
| SW              | 1a             | −2.28*       | DV 5555-6-7777 | 1a             | −1.31        |
|                 | 2a             | −2.04        |                | 2a             | −2.05*       |
|                 | 3a             | −1.56        |                | 3a             | −1.76        |
|                 | 4a             | −1.47        |                | 4a             | −1.48        |
|                 | 5a             | −1.88        |                | 5a             | −1.37        |
| SV              | 1a             | −4.56*       | DV 5-8-5       | 6a             | −1.79        |
| DV 5-8-5        | 1a             | −1.54        |                | 7a             | −1.85        |
|                 | 2a             | −2.31*       |                | 8a             | −1.40        |
| DV 555-777      | 1a             | −1.24        |                | 9a             | −1.25        |
|                 | 2a             | −2.55*       |                |                |              |
|                 | 3a             | −1.95        |                |                |              |
|                 | 4a             | −1.66        |                |                |              |
|                 | 5a             | −1.57        |                |                |              |

The letters in the “adsorption site” columns of the table represent different adsorption zones, and the numbers represent different adsorption sites of each zone.
adsorption at these defects is different. For SW defects, there are 10 carbon atoms each with 1 unpaired electron, so altogether, 10 hydrogen atoms can be adsorbed. For DV defects, there are 8, 9, and 10 unpaired electrons at DV5-8-5, 555-777, and 555-6-7777 defects, respectively. Thus, the number of hydrogens that can be adsorbed at these defects is 8, 9, and 10, respectively.

According to the magnitude of the adsorption energy obtained, the most energetically favored adsorption pathway was identified in the order of (a–j) in Figure 4, and the corresponding adsorption energy of each step is listed in Table 3. At SV and DV5-8-5 defects, the H atoms were adsorbed on the adsorption sites of the SV defect in the order 1a → 1b → 1c → 1a → 1b → 1d → 1c. The adsorption mechanisms of SV and DV5-8-5 defects are similar to the edges. The H atoms were adsorbed at adjacent adsorption sites until each adsorption site adsorbed a H atom. Subsequently, these sites adsorbed a second H atom until each adsorption site absorbed two H atoms. As for SW, DV555-777, and DV555-6-7777, each adsorption site adsorbed only one H atom. It can be found that when a hydrogen was adsorbed at the carbon site, the charge density of the site around that site increased (see Figure 3), making it easier to adsorb the next hydrogen atom. Thus, hydrogen atoms like to adsorb next to the sites where hydrogen atoms are already adsorbed, and finally, the hydrogen and carbon atoms formed a polymer-like structure, which resembled the research of Dzhurakhilov and Peeters.

According to Table 3, the adsorption energies of hydrogen on the interior defects fall into two categories, large $E_{\text{ad}}$ for the saturation of the dangling bonds and smaller $E_{\text{ad}}$ for binding to the π-cloud.

In order to evaluate the relative stability of the structure obtained after adsorption, the Gibbs free energies of each structure were calculated. At a given absolute temperature ($T$), the lines of ($G$) and partial pressure ($P$) are plotted in Figure 5. At the same $T$ and $P$, the lower the $G$ value is, the more stable the structure is. Figure 5 shows the relation between $G$ and $P$ at $T = 300, 600, 900, and 1200$ K. It can be concluded from Figure 5 that at a normal temperature (300 K) and normal partial H pressure (the partial H pressure in air is approximately $5 \times 10^{-7}$ bar), the most stable interior defect structures after hydrogen adsorption are SV + 3H (SV defects adsorb three H atoms) and DV5-8-5 + 4H (DV5-8-5 defects adsorb four H atoms).

Table 3. Adsorption Energies ($E_{\text{ad}}$) of the Best Adsorption Pathways by Increasing H Atoms on the Adsorption Sites of Interior Defects (See Figure 1 to Identify the Positions)$^a$

| system     | ordinal of H | adsorption site | $E_{\text{ad}}$ (eV) | system     | ordinal of H | adsorption site | $E_{\text{ad}}$ (eV) |
|------------|--------------|-----------------|----------------------|------------|--------------|-----------------|----------------------|
| SV         | 1st          | 1a              | −4.56                | DV 555-777 | 1st          | 2a              | −2.55                |
|            | 2nd          | 1b              | −3.14                |            | 2nd          | 2e              | −2.30                |
|            | 3rd          | 1c              | −4.00                |            | 3rd          | 3a              | −1.42                |
|            | 4th          | 1a              | −2.70                |            | 4th          | 3f              | −2.03                |
|            | 5th          | 1c              | −2.00                |            | 5th          | 3e              | −1.65                |
|            | 6th          | 1b              | −1.79                |            | 6th          | 3d              | −2.08                |
|            | 7th          | 1c              | −2.28                |            | 7th          | 3b              | −1.89                |
|            | 8th          | 1b              | −2.51                |            | 8th          | 3c              | −2.33                |
|            | 9th          | 2a              | −1.53                | DV 555-6-7777 | 1st          | 2a              | −2.05                |
|            | 10th         | 2d              | −2.36                |            | 2nd          | 2b              | −2.31                |
|            |              |                 |                      |            | 3rd          | 3a              | −1.72                |
|            |              |                 |                      |            | 4th          | 3d              | −2.01                |
|            |              |                 |                      |            | 5th          | 4a              | −1.96                |
|            |              |                 |                      |            | 6th          | 4d              | −2.18                |
|            |              |                 |                      |            | 7th          | 3c              | −1.34                |
|            |              |                 |                      |            | 8th          | 3b              | −1.86                |
|            |              |                 |                      |            | 9th          | 4c              | −1.85                |
|            |              |                 |                      |            | 10th         | 4b              | −2.15                |

$^a$The letters in the “adsorption site” columns of the table represent different adsorption zones, and the numbers represent different adsorption sites of each zone.
adsorb four \( H \) atoms). For the SW, DV555-777, and DV5555-6-7777 defects, the structure absorbing one hydrogen is the most stable at 300 K. The hydrogenation level increases with the \( H \) partial pressure and decreases with the temperature.

In brief, compared to the perfect graphite surface, the adsorption of hydrogen on the graphite edges and interior defects is much more stable, and the adsorption on the ZZ edge\(^{15}\) and SV defect is more energetically favorable than other structures. The \( H \) atoms are adsorbed at adjacent adsorption sites until each adsorption site adsorbs a \( H \) atom. After that, each adsorption site at SV and DV5-8-5 defects would adsorb the second hydrogen, which is similar to the edges. However, the adsorption sites of SW, DV555-777, and DV5555-6-7777 adsorb only one \( H \) atom. Hydrogen atoms prefer to adsorb next to the sites where hydrogen atoms were already adsorbed and then form polymers. At normal temperature and partial \( H \) pressure, especially in environments where hydrogen (or tritium) is released, the edges absorbing four and eight \( H \) atoms\(^{15}\), SV absorbing three \( H \) atoms, and DV5-8-5 absorbing four \( H \) atoms are the most stable. The adsorption of edges adsorbing eight \( H \) atoms has already been simulated in our previous research\(^{15}\); therefore, in the following study, the edges absorbing four \( H \) atoms, SV + 3\( H \), and DV5-8-5 + 4\( H \) were

Figure 4. Best adsorption pathways of interior defects: (A) SW, (B) SV, (C) DV5-8-5, (D) DV555-777, and (E) DV5555-6-7777. The adsorption process of hydrogen is carried out in the order (a–j).
selected as the initial structures in the following simulation of desorption.

2.3. Desorption. The simulation of hydrogen desorption from nuclear graphite is particularly important in order to remove tritium. For desorption from the edges absorbing four H atoms, there are two types of desorption paths. First, hydrogens on carbon 1 and 2 sites (see Figure 1) are desorbed, which is denoted as 12 desorption. Second, hydrogens on carbon 2 and 3 sites (see Figure 1) are desorbed, which are denoted as 23 desorption. As for interior defects, there are two types of desorption paths (1a1b and 1a1d desorption) for DV5-8-5 defects and one type of desorption path (1b1c desorption) for SV defects. Starting from the most energetically favored adsorption structure obtained, all possible desorption pathways were simulated, and the corresponding potential barriers ($\Delta E_P$) for desorption are shown in Table 4.

The $\Delta E_P$ of 12 desorption for the edges absorbing four H atoms is lower than that for 23 desorption, which is different from the edges absorbing eight H atoms. The only possible desorption pathway for the edges absorbing for H atoms is 12 desorption. Similarly, the only possible desorption pathway for DV5-8-5 absorbing four H isotopes atoms is 1a1b desorption with the lowest desorption potential barrier.

The activation energies ($E_{ac}$) after ZPE correction were calculated and are listed in Table 5. Taking into account the simulation results in our previous study, three different hydrogen-isotope desorption stages with different desorption activation energies can be identified. As shown in Figure 6, in the first stage, hydrogen atoms desorbed from the AC and ZZ edges adsorbing eight H atoms ($E_{ac} = 1.11−1.36$ eV); in the second stage, hydrogen atoms desorbed from the reconstructed armchair (ACR) and reconstructed zigzag (ZZR) edges adsorbing eight H atoms ($E_{ac} = 3.10−3.27$ eV); in the third stage, hydrogen atoms desorbed from the edges adsorbing four H isotopes atoms and interior defects ($E_{ac} = \ldots$)
4.33–5.79 eV). In the three stages, the $E_{ac}$ of deuterium and tritium is slightly higher than that of hydrogen.

2.4. Experimental Section. In a thorium-based molten salt reactor (TMSR), tritium is mainly produced by $^6$Li after absorbing neutrons in the coolant. Part of the resultant tritium is trapped in the coolant, and a larger portion is directly absorbed by structural materials made of nuclear graphite. Therefore, tritium within nuclear graphite will be a great concern when decommissioning the irradiated nuclear graphite. NG-CT-10 nuclear graphite is a potential moderator and a structural material in the high temperature gas-cooled reactors (HTGRs) and thorium-based molten salt reactors (TMSRs) in China. In order to gain an insight into the tritium behavior in the potential nuclear graphite to be used, samples of NG-CT-10 nuclear graphite were subjected to D$_2$ desorption experiments. The gas charging was carried out in D$_2$ gas, and then thermal desorption spectrometry (TDS) spectra released from the gas-charged samples were measured up to 1773 K at a heating rate ranging from 0.03 to 0.15 K/s. A typical TDS spectrum at a heating rate of 0.1 K/s is shown in Figure 7.

A major peak around 1400 K can be found from all spectra, which can be also observed in other spectra obtained from other similar research studies. In order to calculate the activation energy of desorption for this peak, the TDS spectra were obtained at different heating rates ranging from 0.03 to 0.15 K/s and the Kissinger method was applied. The results are shown in Figure 8.

The Kissinger plot shows a great linear relation. Based on the gradient obtained and the Polanyi–Wigner transport equation, the activation energy for the major peak was estimated to be 3.16 eV. The result agrees well with other similar research studies, and most significantly, it matches the activation energy calculated for the deuterium desorbed from the graphite edge. Therefore, the results from our experiments and simulation indicate that the major peak around 1400 K in the TDS spectrum originates from the desorption of hydrogen isotopes absorbed at the reconstructed edge of the graphite crystallite.

Apart from the major peak whose peak temperature is around 1400 K, more peaks can be found at higher temperatures. Since these peaks overlap with each other most of the time at various heating rates, the estimation of the activation energy was not attempted. However, our simulation showed a series of hydrogen desorption pathways with high activation energies (4.33–5.79 eV), which could give a reasonable explanation for the peak with a peak temperature higher than 1400 K. Moreover, the phenomenon of multiple

| system | $\Delta E_p$ (eV) | $\Delta E_{	ext{ZPE}}$ (eV) | $E_{ac}$ (eV) |
|--------|-----------------|-----------------|-------------|
| 4H     |                 |                 |             |
| AC     | 5.08            | 0.21            | 4.87        |
| ACR    | 6.66            | 0.31            | 4.35        |
| ZZ     | 5.97            | 0.31            | 5.66        |
| ZZR    | 4.67            | 0.18            | 4.49        |
| 3H     | 4.60            | 0.27            | 4.33        |
| 4H     | 5.20            | 0.24            | 4.96        |

Figure 6. Three different hydrogen-isotope desorption stages.

Figure 7. Typical TDS of deuterium release from NG-CT-10 with a heating rate of 0.1 K/s.

Figure 8. Kissinger plot for the major peak in TDS.
peaks at high temperature was also reported by Atsumi (2018).\textsuperscript{23} In spite of the peak found at an elevated temperature, Atsumi (2017)\textsuperscript{22} reported another peak at a lower temperature around 600 K, which can be explained as the hydrogen desorption from closed pores. With reference to our simulation results, although the peak at the lower temperature cannot be found in the TDS spectrum, the peak could also be due to the desorption of hydrogen from the graphite edge without reconstruction.

3. CONCLUSIONS

In summary, the graphite edge absorbing four H atoms and internal defects were studied based on the DFT to comprehensively understand the adsorption and desorption behaviors of hydrogen isotopes in nuclear graphite. The adsorption mechanisms of SV and DV5-8-5 defects are similar to those of the edges, and each adsorption site can adsorb two H atoms. However, the adsorption sites of other interior defects can absorb only one H atom. Hydrogen atoms tend to adsorb next to the sites at which hydrogen atoms were already adsorbed and then form polymers. At a reasonable temperature and hydrogen pressure, the edges absorbing four and eight H atoms, SV + 3H and DV5-8-5 + 4H, are the most energetically favorable. Moreover, the $E_{\text{ad}}$ of hydrogen isotopes desorbing from the edges absorbing four H atoms, SV + 3H, and DV5-8-5 + 4H were calculated. The activation energy calculated was higher than the activation energy when hydrogen desorbed from the crystallite edge, implying that a higher temperature was required to remove the hydrogen adsorbed at these interior defects.

The experiment of TDS was carried out to estimate the desorption activation energy of deuterium desorbed from nuclear graphite. The activation energy estimated from TDS for the major peak around 1400 K agrees well with our simulation result for the hydrogen isotopes desorbed from the reconstructed graphite edge. Apart from the major peak, more peaks can be found at higher temperature, which correspond to the desorption of hydrogen isotopes from interior defects. The desorption peak at lower temperature was not found in our TDS spectrum.

This work provides a deeper understanding of the adsorption and desorption behaviors of hydrogen isotopes on graphene and provides a theoretical basis for the decontamination of nuclear graphite.

4. COMPUTATIONAL AND EXPERIMENTAL METHODS

4.1. Calculation Method. Based on DFT,\textsuperscript{25–27} this work used the \textit{ab initio} total-energy code Vienna \textit{ab initio} simulation package.\textsuperscript{15,26,29} The correlation interactions were described by the projected augmented wave\textsuperscript{29} and the generalized gradient approximation of Perdew, Burke, and Ernzerhof.\textsuperscript{30,31} The cutoff energy of the plane-wave basis was 450 eV.\textsuperscript{17} The energy convergence criterion was $10^{-6}$ eV, and the $k$-point was a grid of $4 \times 4 \times 1$. This study used the climbing-image nudged elastic band to find the pathways with a minimum energy.\textsuperscript{32,33} The lattice constant of the optimized perfect graphene (2.460 Å) agrees well with the theoretical and experimental results.\textsuperscript{5,2,26}

The adsorption energy ($E_{\text{ad}}$) is defined as the energy difference between the energy of the hydrogen-passivated and the nonpassivated defect graphene and a hydrogen, which is expressed as

$$E_{\text{ad}} = E^\text{tot} - E^\text{defect graphene} - N_H E^H$$

where $E^\text{tot}$ and $E^\text{defect graphene}$ are the total energies of the hydrogen-passivated and the nonpassivated defect graphene, respectively, and $E^H$ is the energy of the isolated hydrogen atom in a free state. $N_H$ is the number of hydrogen atoms in the supercell.

The desorption active energy ($E_{\text{des}}$) is the potential barrier ($\Delta E_p$) after the vibrational zero-point energy ($E_{\text{zpe}}$) correction.\textsuperscript{15}

The formation energy is expressed as

$$\epsilon = E^\text{tot} - N_C E^\text{graphene} - N_H E^H$$

where $E^\text{tot}$, $E^\text{graphene}$, and $E^H$ are the total energy of hydrogen-passivated defect graphene, the energy of a carbon atom in graphene, and the energy of the isolated hydrogen atom in the freedom state, respectively. $N_C$ and $N_H$ are the number of carbon and hydrogen atoms in the supercell.

At a given chemical potential $\mu_H$, the relative stability is obtained by comparing $G$.

$$\mu_H = H^\circ(T) - H^\circ(0) - TS^\circ + k_B T \ln \left( \frac{P}{P_0} \right)$$

$$G = \epsilon - N_H \left( H^\circ(T) - H^\circ(0) - TS^\circ + k_B T \ln \left( \frac{P}{P_0} \right) \right)$$

where $T$ is the absolute temperature, $P$ is the partial hydrogen pressure, and $H^\circ (S^\circ)$ is the enthalpy (entropy) at the pressure $P_0 = 1 \text{ bar}$.\textsuperscript{34} At the same $T$ and $P$, the lower the $G$ value is, the more stable the structure is.

4.2. Experimental Method. NG-CT-10 nuclear graphite, which was manufactured by China Fangda Carbon Company, Ltd., was subject to D$_2$ desorption experiments. The sample was outgassed at 1773 K for 2 h prior to gas charge. The gas charging was carried out in D$_2$ gas at 1273 K for 10 h. The TDS spectra released from the gas-charged samples were measured up to 1773 K at a heating rate ranging from 0.03 to 0.15 K/s with a quadrupole mass spectrometer (LC-D200M, AMETEK Ltd.).

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (grant no. 21906164).

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