

Xi-Jun Wu^{1,2} · Ze-Jie Fei² · Wen-Guan Liu² · Jie Tan³ · Guang-Hua Wang² · Dong-Qin Xia⁴ · Ke Deng² · Xue-Kun Chen¹ · De-Tao Xiao¹ · Sheng-Wei Wu² · Wei Liu²

Received: 26 July 2018/Revised: 19 September 2018/Accepted: 19 October 2018/Published online: 25 March 2019 © China Science Publishing & Media Ltd. (Science Press), Shanghai Institute of Applied Physics, the Chinese Academy of Sciences, Chinese Nuclear Society and Springer Nature Singapore Pte Ltd. 2019

Abstract Adsorption and desorption of hydrogen on/from single-vacancy and double-vacancy graphenes were studied by means of first-principles calculations. The structure and stability of continuous hydrogenation in single vacancy were investigated. Several new stable structures were found, along with their corresponding energy barriers. In double-vacancy graphene, the preferred sites of H atoms were identified, and H_2 molecule desorption and adsorption of from/on were calculated from the energy barriers. This work provides a systematic and comprehensive understanding of hydrogen behavior on defected graphene.

This work is supported by the National Natural Science Foundation of China (Grant No. 51601212; 11475082) and "Strategic Priority Research Program of Chinese Academy of Sciences" Thorium Molten Salts Reactor Fund.

Wen-Guan Liu liuwenguan@sinap.ac.cn

Sheng-Wei Wu wushengwei@sinap.ac.cn

Xi-Jun Wu wuxijunusc@163.com

- ¹ School of Mathematics and Physics, University of South China, Hengyang 421001, China
- ² Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China
- ³ Sino-French Institute of Nuclear Engineering and Technology, Sun Yat-Sen University, Zhuhai 519082, Guangdong, China
- ⁴ Key Laboratory of Neutronics and Radiation Safety, Institute of Nuclear Energy Safety Technology, Chinese Academy of Sciences, Hefei 230031, Anhui, China

Keywords Hydrogen \cdot Graphene \cdot Single vacancy \cdot Double vacancy \cdot Adsorption \cdot Desorption \cdot First-principles calculation

1 Introduction

Storage of hydrogen, as one of the clean alternative energy resources with highest energy content by weight [1], has been investigated in metal hydrides [2, 3], alloys [4-7], and porous substances [8, 9] and is found to be particularly promising in graphene [10–20], which has excellent electronic, mechanical, and thermal properties [21, 22], as well as the special characteristic of reversible hydrogenation–dehydrogenation reactions [23]. The hydrogen isotope tritium is one of the most important initial radiological activities of irradiated graphite waste after reactor shutdown [23], and therefore, tritium desorption from such phenomenon becomes one of the crucial targets of decontamination of nuclear graphite. Tritium has adsorption, diffusion, and desorption properties similar with hydrogen; for this reason, fundamental understanding of the adsorption/desorption of hydrogen molecules and the migration mechanism of H atoms on graphene surface is of particular importance [24].

Nevertheless, the dissociation rate of H_2 molecules on pristine graphene is too low as it goes through physisorption, while the dissociation energy barrier is very high (2.7–3.3 eV) [25, 26]. Compared to pristine graphene (or graphene-like materials), adsorption and desorption of H_2 are easier on graphene (or graphene-like materials) with defects [24, 27–37]. Nonetheless, such various defects, including the adsorption property of electromagnetic waves [38–40], dielectric property [41], and so on, affect the



properties and performance of graphene. Studies have shown that the adsorbing capacity of toxic gases (NO, CO, HCN, and SO₂) [42] and reactive gases (CO and O₂) [43–46] on graphene (or graphene-like materials) can be regulated by doping and that vacancies as common defects reduce the adsorption energy of adsorbents, such as sodium [47] and H atoms [48], so that graphenes with vacancy defects have attracted considerable research attention [28–37]. Vacancy defects in graphene can enhance its reactivity and affect charge distributions and are always found to be sites of chemisorption [24]; they are classified into single vacancy (SV), double vacancy (DV), among others [49–52].

SV is identified to promote the dissociation of H₂ molecules with reduced activation barrier energy of 0.63 eV, as compared to 2.38 eV for pristine graphene [53]. An isolated SV in a graphene can bind four H atoms stably or even six, to form a metastable and magnetic structure at room temperature [53]. On one hand, successive adsorption reaction of H₂ on SV has been studied [48, 54, 55], especially in Ref. [48], where a detailed map of the continuous process of hydrogenation was demonstrated systematically. On the other hand, the reversible hydrogenation-dehydrogenation reactions have been discussed in Sunnardianto et al., who reported on a reversible hydrogen-dissociative adsorption on a SV graphene that absorbs two H atoms [55]; they further stated minimum energy pathways and activation barriers for both adsorption and desorption of one H₂ molecule on triple-hydrogenated vacancy graphene that suggests a potential application for hydrogen storage [56].

The focus of previous research to date was on SV graphene, while rare attention has been paid to DV graphene, which has better thermal stability, and thus is thermodynamically favored over the former, aside from its vacancies having even number of missing atoms being more stable than those with odd number of missing atoms [49–51]. In this paper, we utilized first-principles calculation to study the behaviors of hydrogen adsorption, diffusion, and desorption on both SV and DV graphenes, which could provide theoretical guidance for both hydrogen storage by use of graphene and thermal desorption of tritum from decommissioned nuclear graphite.

2 Computational methods

All calculations were performed via density functional theory method [57, 58] implemented in the Vienna Ab initio Simulation Package (VASP) [59]. Exchange and correlation effects were treated self-consistently with a generalized gradient approximation (GGA) [60]. To describe the electron–ion interaction, the projector

augmented wave (PAW) pseudo-potential [61] was employed. Cutoff energy for the plane wave basis was set at 450 eV to ensure good convergence. Geometry optimization was performed with force convergence criterion of 0.01 eV/Å, while energy convergence criterion was 10^{-6} eV. Diffusion and desorption energy barriers were estimated through the climbing image nudged elastic band (CI-NEB) method [62-64]. The Brillouin zone was sampled with a grid of $4 \times 4 \times 1$ k-points, with the lattice constant of optimized graphene set to 2.462 Å, which is in good agreement with other theoretical and experimental values [65, 66]. A 6×6 hexagonal supercell containing 72 carbon atoms was used to model the graphene in all the calculations. Periodic boundary conditions were adopted in all three directions, and the size of supercell in the z-axis (i.e., the thickness of the vacuum) was set at 18.75 Å.

The reaction energy for adsorbing n H atoms on the graphene is computed as [48]

$$\Delta E_n = E_{\rm VH_n} - E_{\rm V} - E_{n\rm H},\tag{1}$$

where the three terms on the right are the total energy of the graphene supercell with *n*-times hydrogenated vacancy, the energy of the graphene supercell with bare vacancy, and the reference state of *n* H atoms, respectively. The reaction energy for sequential adsorption $\Delta\Delta E_n$ is defined similarly as [48]

$$\Delta \Delta E_n = \Delta E_n - \Delta E_{n-1} = E_{\mathrm{VH}_n} - E_{\mathrm{VH}_{n-1}} - E_{\mathrm{H}}, \qquad (2)$$

where ΔE_{n-1} refers to the (n-1)-times hydrogenated state.

As validation, we simulated the adsorption, migration, and desorption behaviors of H atoms on pristine graphene. Results showed an adsorption energy of 0.73 eV, which agrees well with the other theoretical values [67, 68], and desorption energy barrier of 2.55 eV, which also coincides with those of previous studies [26, 69].

3 Results and discussion

3.1 SV and DV graphene structures

The calculation model of the SV graphene was constructed from a carbon atom extracted from the 6×6 hexagonal supercell; then, the bare vacancy underwent a Jahn–Teller distortion, with two of the three carbon atoms in it forming a C–C bond [50, 70–73]. Likewise, the DV graphene model was formed from the 6×6 hexagonal supercell by extracting two carbon atoms in different ways. Calculation models of SV, DV5-8-5, DV555-777, and DV5555-6-7777 graphenes [49–52] after structure optimization are shown in Fig. 1. The simplest DV graphene was DV5-8-5, which contains two pentagons and one



Fig. 1 Schematic diagram for different adsorption sites on a SV defect, b DV of 5-8-5 defect, c DV of 555-777 defect, and d DV of 5555-6-7777 defect. Numbers on the structures indicate stable adsorption sites with high symmetry; the dash lines in DV indicate structural symmetry

octagon; the most stable was DV555-777 [74] with three pentagons and three heptagons; DV5555-6-7777 had four pentagons, one hexagon, and four heptagons. No dangling bonds were present in these three DV structures unlike in the SV structure. Simulation results illustrated that the top site of the carbon atom in the DV structures was a stable adsorption site.

3.2 Hydrogen adsorption and desorption on SV graphenes

Figure 2 shows a detailed map of optimized hydrogenated SV graphene structures, in which the calculated energies were compared with the results in Ref. [48] (shown in blue inside parentheses in Fig. 2). Only the energetically favorable process of continuous hydrogenation in SV graphene is depicted in the figure.

In general, the resulting adsorption energies in Fig. 2 coincide with those in Ref. [48]. In the SV graphene, a first H atom was preferentially absorbed by the C atom with a dangling bond, i.e., C1 in Fig. 1a, which is strongly exothermic, and the adsorption energy was -4.35 eV, slightly higher than -4.42 eV [48], but significantly lower than -3.45 eV [53]. When adsorbing a second H atom, along with the initial atom, they could be located either on the same or on different sides, with the most energetically favorable configuration labels of SV_{11(u-u)} and SV_{11(u-d)}. After absorption of a third H atom, the most stable structure becomes SV_{111(u-u-d)}. (Each of the three vacant C atoms bonding with one H atom and one of the three H atoms are oriented differently.)

From Fig. 2, the SV_{111(u-u-d)} configuration could transform into SV_{211(ud-d-d)} through adsorption of a fourth H atom at -2.42 eV, which again agrees with Ref. [48]. Nevertheless, SV_{111(u-u-d)} was also found to transform to SV_{211(uu-u-d)} by adsorbing a fourth H atom at the energy of -2.71 eV, which is not found in Ref. [48] and which was even lower than that in SV_{211(ud-d-d)} (-2.42 eV), so that SV_{211(uu-u-d)} was as important as SV_{211(ud-d-d)}. Unfortunately, the SV_{211(uu-u-d)} configuration is yet to be studied.

After absorption of the fifth H atom, $SV_{221(ud-ud-u)}$, $SV_{221(uu-ud-d)}$, and $SV_{221(uu-uu-d)}$ form, as demonstrated in Fig. 2. Desorption of hydrogen molecule from $SV_{221(ud-ud-u)}$ to form SV_{111} and, in turn, adsorption of hydrogen molecule in SV_{111} to form $SV_{221(ud-ud-u)}$ have been investigated in Ref. [56], in which the energy barrier of these reactions was 1.3 eV, which means this storage and release concept has the potential to act as a hydrogen storage system. Furthermore, in this work, first-principles calculations were used to study the energy pathways and barriers of the reactions, i.e., $SV_{111} + H_2 \leftrightarrow SV_{221(uu-ud-d)}$.

Minimum energy pathways for $SV_{221(uu-ud-d)} \leftrightarrow SV_{111(u-d-d)} + H_2$ and $SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2$ are shown in Fig. 3. The energy barriers of H_2 desorption and adsorption for $SV_{221(uu-ud-d)} \leftrightarrow SV_{111(u-d-d)} + H_2$ and for $SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-d-d)} + H_2$ and for $SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2$ were 1.85 eV and 1.92 eV, and 2.17 eV and 2.26 eV, respectively. All energy barriers of these two reactions were apparently higher than those for $SV_{221(ud-ud-u)} \leftrightarrow SV_{111(u-u-d)} + H_2$ (i.e., 1.30 eV [56]), but their desorption energy barriers were lower than those for $SV_{2(u-u)} \rightarrow SV + H_2$ (i.e.,



Fig. 2 Energetically favorable process of continuous hydrogenation in SV graphene, with adsorption energies $\Delta\Delta E_n$ (eV), as compared with the results from Ref. [48] (i.e., values in blue font). The subscript of SV denotes the amount of H atoms adsorbed to its C atoms; the

terms "u" and "d" represent the up and down configurations of H, respectively. Hydrogenated SV structures in gray and yellow colors found to be relatively stable in Ref. [48]



(1) $SV_{221}(uu-ud-d) \leftrightarrow SV_{111}(u-d-d) + H_2$

(2) $SV_{221}(uu-uu-d) \leftrightarrow SV_{111}(u-u-d) + H_2$

 $\textbf{Fig. 3} \hspace{0.1in} \text{Minimum energy pathways for } \textbf{a} \hspace{0.1in} SV_{221(uu-ud-d)} \leftrightarrow SV_{111(u-d-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} \leftrightarrow SV_{111(u-u-d)} + H_2, \hspace{0.1in} \text{and } \textbf{b} \hspace{0.1in} SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} \leftrightarrow SV_{11(u-u-d)} \leftrightarrow SV_{11(u-u-$

4.06 eV [53]), and their adsorption energy barriers were significantly higher than those for SV + H₂ \rightarrow SV_{2(u-u)} (i.e., 0.63 eV [53]). As a result, H₂ desorption and adsorption were more difficult in SV_{221(uu-ud-d)} \leftrightarrow SV_{111(u-d-d)} + H₂ and SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-d-d)} + H₂ and SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H₂, and these two reactions could not be identified as potential hydrogen storage reactions.

3.3 Adsorption, migration, and desorption of hydrogen on DV graphene

Figure 1 illustrates the stable adsorption sites with high symmetry in DV5-8-5, DV555-777, and DV5555-6-7777. Adsorption energies of hydrogen in these sites were calculated and are given in Table 1, where the adsorption energies of H atoms observed on the DV region were mostly lower than those away from the region. For

Table 1 Adsorption energies, E_{ad} , of an H atom on the stable adsorption sites with high symmetry in DVs (see Fig. 1 to identify the positions)

Substrates	Sites	$E_{\rm ad}~({\rm eV})$
DV5-8-5	T ₁	- 1.22
	T_2	- 2.31
	T ₃	- 1.57
	T_4	- 1.23
	T_5	- 0.97
	T_6	- 1.23
	T ₇	- 1.65
	T_8	- 1.18
DV555-777	T_1	- 1.18
	T_2	- 2.51
	T ₃	- 1.95
	T_4	- 1.86
	T ₅	- 1.60
	T_6	- 1.31
DV5555-6-7777	T_1	- 1.40
	T_2	- 2.14
	T ₃	- 1.82
	T_4	- 1.51
	T ₅	- 1.47
	T_6	- 1.83
	T ₇	- 1.90
	T_8	- 1.53
	T_9	- 1.33
	T ₁₀	- 1.12

example, the adsorption energy of an H atom in T_2 site of DV555-777 (i.e., -2.51 eV) was apparently lower than in the T_6 site (i.e., -1.31 eV). This indicated that H atoms have an evident tendency to diffuse to the region of double vacancy from outside. The adsorption, migration, and desorption behaviors of H atoms in these DVs were studied and are shown in Figs. 4, 5, and 6.

In DV5-8-5, the region of double vacancies mainly had an octagon ring and two pentagon rings; in DV555-777, the vacancy region was made up of three octagon and three pentagon rings; in DV5555-6-7777, the region was composed of four octagon and two pentagon rings, and one hexagon ring. Hence, the order of the vacancy size was DV5555-6-7777 > DV555-777 > DV5-8-5, which could influence the capacity of hydrogen adsorption on these structures.

According to the calculated adsorption energies in Table 1, the most stable site in DV5-8-5 was T_2 , as shown in Figs. 1b and 4, which was the top site of the carbon atom shared by a pentagon, a hexagon, and an octagon ring. Hydrogen adsorption energy in this site was -2.31 eV, and the first adsorbed H atom was bound to occupy this site. The second most stable site in DV5-8-5 was not T_1 in the octagon ring, but T_3 with adsorption energy of -1.57 eV. It was clear from Table 1 that the adsorption sites (e.g., T_2 and T_3) in DV5-8-5 were more stable than those away from the vacancy (e.g., T_8), which justified the tendency of H atoms to accumulate in the vacancy region of DV5-8-5.

Adsorption and desorption of H₂ molecules on/from DV5-8-5 are shown in Fig. 4. Before the desorption process, two H atoms should gather together in the DV5-8-5; the first atom was adsorbed in T₂, while the second was assumed to migrate along the path of $T_5 \rightarrow T_4 \rightarrow T_3$ to T_3 , which is the second most stable site. Two steps occurred during this migration at energy barriers of 1.21 eV and 0.49 eV, as shown in Fig. 4. The possible desorption of H_2 molecule from DV5-8-5 was investigated, where the system energy decreased by 0.21 eV after dehydrogenating; Nevertheless, the reaction energy barrier was found to be 2.10 eV, which means that desorption of H₂ molecule was difficult. For the adsorption of H₂ molecule on DV5-8-5, the energy barrier was 2.31 eV, close to the value on pristine graphene (i.e., 2.38 eV) [53], which is mainly induced by the absence of dangling bonds in both DV5-8-5 and pristine graphene.

From Table 1, the most stable site in DV555-777 was that of T_2 at adsorption energy of -2.51 eV. Interestingly, T_2 was not the center of DV555-777, as shown in Fig. 1; the center site T_1 , however, was the most energetically unfavorable energetically, as observed in Table 1, with adsorption energy of -1.18 eV.



Fig. 4 Schematic diagram of adsorption and desorption of H_2 molecule on DV5-8-5 graphene surface. The energy value of the first structure on the left is designated at zero. Desorption process is from left to right, while adsorption process is in the opposite direction



Fig. 5 Schematic diagram of H_2 molecule adsorption and desorption on DV555-777 graphene surface. The energy value of the first structure on the left is designated at zero. Desorption process is from left to right, while adsorption process in the opposite direction



Fig. 6 Schematic diagram of adsorption and desorption of H_2 molecule on DV5555-6-7777 graphene surface. The energy value of the first structure on the left is designated at zero. Desorption process is from left to right, while adsorption process in the opposite direction

Figure 5 shows the adsorption and desorption of H_2 molecules on/from DV555-777. The first H atom was adsorbed in T_2 , while the second was supposed to diffuse along the path of $T_6 \rightarrow T_4 \rightarrow T_3$ to T_3 , which was the second most stable site and was adjacent to T_2 . From the figure, the energy barriers of the two-step migration were 0.74 eV and 0.71 eV, respectively. The energy barriers of H_2 desorption and adsorption were calculated at 2.23 eV and 2.55 eV, respectively. Hence, while migration for H_2 molecule was relatively easy, desorption and adsorption from/on DV555-777 were otherwise difficult.

For the configuration of DV5555-6-7777 in Table 1, T_2 was the most stable site with -2.14 eV energy of adsorption, and thus, the first H was adsorbed in this site. The second H was assumed to migrate through T_{10} . $\rightarrow T_4 \rightarrow T_3$ to T_3 , which was a relatively stable site adjacent to T_2 , and the corresponding energy barriers were 0.69 eV and 0.97 eV, respectively, as shown in Fig. 6. As in the cases of DV5-8-5 and DV555-777, H₂ molecule adsorption and desorption from/on DV5555-6-7777 was also difficult, because the energy barriers for these processes were 2.10 and 2.76 eV, respectively, as in Fig. 6.

4 Conclusions

First-principles calculations were performed for investigation of adsorption and desorption processes of hydrogen from SV and DV graphenes. In SV graphene, continuous hydrogenation was an energetically favorable process, and the minimum energy pathways were calcu- $SV_{221(uu-ud-d)} \leftrightarrow SV_{111(u-d-d)} + H_2$ lated by and $SV_{221(uu-uu-d)} \leftrightarrow SV_{111(u-u-d)} + H_2$. In DV graphene, adsorption energies of H atoms on the region of double vacancy were generally lower than those away from the region, and the corresponding energy barriers for H diffusion into the vacancy were relatively low as well. Based on these energy barriers, desorption and adsorption of H₂ molecules from/on DV graphenes were difficult. This work provides a comprehensive understanding of adsorption and desorption of hydrogen on/from single-vacancy and double-vacancy graphenes, and can serve as theoretical guidance for both hydrogen storage on graphene and thermal desorption of tritium from decommissioned nuclear graphite.

References

- 1. I. Staffell, The energy and fuel data sheet. 2011. http://tinyurl. com/energydata
- P.D. Jongh, M. Allendorf, J.J. Vajo et al., Nanoconfined light metal hydrides for reversible hydrogen storage. MRS Bull. 38, 488–494 (2013). https://doi.org/10.1557/mrs.2013.108
- L. Pickering, J. Li, D. Reed et al., Ti–V–Mn based metal hydrides for hydrogen storage. J. Alloys Compd. 580, 233–237 (2013). https://doi.org/10.1016/j.jallcom.2013.03.208
- A.M. Jorge, E. Prokofiev, G.L. de Lima et al., An investigation of hydrogen storage in a magnesium-based alloy processed by equalchannel angular pressing. Int. J. Hydrogen Energy 38, 8306–8312 (2013). https://doi.org/10.1016/j.ijhydene.2013.03.158
- D.L. Chao, C.L. Zhong, Z.W. Ma et al., Improvement in hightemperature performance of Co-free high-Fe AB 5-type hydrogen storage alloys. Int. J. Hydrogen Energy **37**, 12375–12383 (2012). https://doi.org/10.1016/j.ijhydene.2012.05.147
- C.N. Peng, The effects of hydrogen on the helium behavior in palladium. Nucl. Sci. Tech. 27, 106 (2016). https://doi.org/10. 1007/s41365-016-0115-5
- W.G. Liu, Y. Qian, D.X. Zhang et al., Theoretical study of the interaction between hydrogen and 4d alloying atom in nickel. Nucl. Sci. Tech. 28, 82 (2017). https://doi.org/10.1007/s41365-017-0235-6
- P. Reunchan, S.H. Jhi, Metal-dispersed porous graphene for hydrogen storage. Appl. Phys. Lett. 98, 93–103 (2011). https:// doi.org/10.1063/1.3560468
- Y. Xia, Z. Yang, Y. Zhu, Porous carbon-based materials for hydrogen storage: advancement and challenges. J. Mater. Chem. A 1, 9365–9381 (2013). https://doi.org/10.1039/c3ta10583k
- X.K. Chen, J. Liu, Z.H. Peng et al., A wave-dominated heat transport mechanism for negative differential thermal resistance in graphene/hexagonal boron nitride heterostructures. Appl. Phys. Lett. 110, 091907 (2017). https://doi.org/10.1063/1.4977776
- X.K. Chen, Z.X. Xie, W.X. Zhou et al., Thermal rectification and negative differential thermal resistance behaviors in graphene/ hexagonal boron nitride heterojunction. Carbon 100, 492–500 (2016). https://doi.org/10.1016/j.carbon.2016.01.045
- M. Pumera, Graphene-based nanomaterials for energy storage. Energy Environ. Sci. 4, 668–674 (2011). https://doi.org/10.1039/ c0ee00295j
- S. Patchkovskii, J.S. Tse, S.N. Yurchenko et al., Graphene nanostructures as tunable storage media for molecular hydrogen. Natl. Acad. Sci. USA **102**, 10439–10444 (2005). https://doi.org/ 10.1073/pnas.0501030102
- D.W. Boukhvalov, M.I. Katsnelson, A.I. Lichtenstein, Hydrogen on graphene: electronic structure, total energy, structural distortions and magnetism from first-principles calculations. Phys. Rev. B 77, 035427 (2008). https://doi.org/10.1103/PhysRevB.77. 035427
- D.C. Elias, R.P. Nair, T.M. Mohiuddin et al., Control of grphene's properties by reversible hydrogenation: evidence for graphane. Science 323, 610–613 (2009). https://doi.org/10.1126/ science.1167130
- R. Balog, B.J. Jorgensen, L. Nilsson et al., Bandgap opening in graphene induced by patterned hydrogen adsorption. Nat. Mat. 9, 315–319 (2010). https://doi.org/10.1038/NMAT2710
- B.S. Pujari, S. Gusarov, M. Brett et al., Single-side-hydrogenated graphene: density functional theory predictions. Phys. Rev. B 84, 041402 (2011). https://doi.org/10.1103/PhysRevB.84.041402
- S.S. Han, H. Jung, D.H. Jung et al., Stability of hydrogenation states of graphene and conditions for hydrogen spillover. Phys. Rev. B 85, 155408 (2012). https://doi.org/10.1103/PhysRevB.85. 155408

- W. Zhou, J. Zhou, J. Shen et al., First-principles study of highcapacity hydrogen storage on graphene with Li atoms. J. Phys. Chem. Solids 73, 245–251 (2012). https://doi.org/10.1016/j.jpcs. 2011.10.035
- V. Tozzini, V. Pellegrini, Prospects for hydrogen storage in graphene. Phys. Chem. Chem. Phys. 15, 80–89 (2013). https:// doi.org/10.1039/c2cp42538f
- S. Gadipelli, Z. Guo, Graphene-based materials: synthesis and gas sorption, storage and separation. Prog. Mater Sci. 69, 1–60 (2015). https://doi.org/10.1016/j.pmatsci.2014.10.004
- H. Hu, J. Xin, H. Hu et al., Metal-free graphene-based catalysteinsight into the catalytic activity: a short review. Appl. Catal. A. Gen. 492, 1–9 (2015). https://doi.org/10.1016/j.apcata.2014.11.041
- M.L. Guillou, N. Toulhoat, Y. Pipon et al., Deuterium migration in nuclear graphite: consequences for the behavior of tritium in CO₂-cooled reactors and for the decontamination of irradiated graphite waste. J. Nucl. Mater. 461, 72–77 (2015). https://doi.org/ 10.1016/j.jnucmat.2015.03.005
- T.N. Hoai, K.H. Lam, N.T. Thanh et al., Migration and desorption of hydrogen atom and molecule on/from graphene. Carbon 121, 248–256 (2017). https://doi.org/10.1016/j.carbon.2017.05.069
- Y. Miura, H. Kasai, W. Dino et al., First principles studies for the dissociative adsorption of H₂ on graphene. J. Appl. Phys. 933, 395–400 (2003). https://doi.org/10.1063/1.1555701
- Z. Ao, S. Li, in *Graphene Simulation*, ed. by J.R. Gong (InTech, Rijeka, 2011), p. 53
- M. Terrones, A.R. Botello-Mendez, J. Campos-Delgado et al., Graphene and graphite nanoribbons: morphology, properties, synthesis, defects and applications. Nano Today 5, 351–372 (2010). https://doi.org/10.1016/j.nantod.2010.06.010
- K.S. Novoselov, A.K. Geim, S.V. Morozov et al., Two-dimensional gas of massless dirac fermions in graphene. Nature 438, 197–200 (2005). https://doi.org/10.1038/nature04233
- K. Nordlund, J. Keinonen, T. Mattila, Formation of ion irradiation induced small-scale defects on graphite surfaces. Phys. Rev. Lett. 77, 699–702 (1996). https://doi.org/10.1103/PhysRevLett. 77.699
- A. Hashimoto, K. Suenaga, A. Gloter et al., Direct evidence for atomic defects in graphene layers. Nature 430, 870–873 (2004). https://doi.org/10.1038/nature02817
- P.O. Lehtinen, A.S. Foster, Y. Ma et al., Irradiation-induced magnetism in graphite: a density functional study. Phys. Rev. Lett. 93, 187202 (2004). https://doi.org/10.1103/PhysRevLett.93. 187202
- O.V. Yazyev, L. Helm, Defect-induced magnetism in graphene. Phys. Rev. B 7, 125408 (2007). https://doi.org/10.1103/Phys RevB.75.125408
- V.M. Pereira, D.S. Lopes, N.A. Castro, Modeling disorder in graphene. Phys. Rev. B 77, 115109 (2008). https://doi.org/10. 1103/PhysRevB.77.115109
- O.V. Yazyev, Magnetism in disordered graphene and irradiated graphite. Phys. Rev. Lett. 101, 037203 (2008). https://doi.org/10. 1103/PhysRevLett.101.037203
- J.C. Meyer, C. Kisielowski, R. Erni et al., Direct imaging of lattice atoms and topological defects in graphene membranes. Nano Lett. 8, 3582–3586 (2008). https://doi.org/10.1021/nl801386m
- M.M. Ugeda, I. Brihuega, F. Guinea et al., Missing atom as a source of carbon magnetism. Phys. Rev. Lett. **104**, 096804 (2010). https://doi.org/10.1103/PhysRevLett.104.096804
- T. Kondo, Y. Honma, J. Oh et al., Edge states propagating from a defect of graphite: scanning tunneling spectroscopy measurements. Phys. Rev. B 82, 153414 (2010). https://doi.org/10.1103/ PhysRevB.82.153414
- 38. B. Wen, M.S. Cao, M.M. Lu et al., Reduced graphene oxides: light-weight and high-efficiency electromagnetic interference

shielding at elevated temperatures. Adv. Mater. **26**, 3484–3489 (2014). https://doi.org/10.1002/adma.201400108

- M.S. Cao, X.X. Wang, W.Q. Cao et al., Thermally Driven Transport and Relaxation Switching Self-Powered Electromagnetic Energy Conversion. Small 14, 1800987–1800994 (2018). https://doi.org/10.1002/smll.201800987
- W.Q. Cao, X.X. Wang, J. Yuan et al., Temperature dependent microwave absorption of ultrathin graphene composites. J. Mater. Chem. C 3, 10017–10022 (2015). https://doi.org/10.1039/c5tc02185e
- W.L. Song, M.S. Cao, Z.L. Hou et al., High dielectric loss and its monotonic dependence of conducting-dominated multiwalled carbon nanotubes/silica nanocomposite on temperature ranging from 373 to 873 K in X-band. Appl. Phys. Lett. 94, 233110 (2009). https://doi.org/10.1063/1.3152764
- 42. Y.N. Tang, Z.Y. Liu, Z.G. Shen et al., Adsorption sensitivity of metal atom decorated bilayer graphene toward toxic gas molecules (CO, NO, SO₂ and HCN). Sensor. Actuat. B Chem. 238, 182–195 (2017). https://doi.org/10.1016/j.snb.2016.07.039
- 43. Y.N. Tang, H.D. Chai, W.G. Chen et al., Theoretical study on geometric, electronic and catalytic performances of Fe dopant pairs in graphene. Phys. Chem. Chem. Phys. 19, 26369–26380 (2017). https://doi.org/10.1039/c7cp05683d
- 44. Y.N. Tang, W.G. Chen, Z.G. Shen et al., Nitrogen coordinated silicon-doped graphene as a potential alternative metal-free catalyst for CO oxidation. Carbon 111, 448–458 (2017). https://doi. org/10.1016/j.carbon.2016.10.028
- 45. Y.N. Tang, H.D. Chai, H.W. Zhang et al., Tuning the adsorption and interaction of CO and O-2 on graphene-like BC3-supported non-noble metal atoms. Phys. Chem. Chem. Phys. 20, 14040–14052 (2018). https://doi.org/10.1039/c8cp00772a
- 46. Y.N. Tang, Z.G. Shen, Y.Q. Ma et al., Divacancy-nitrogen/boroncodoped graphene as a metal-free catalyst for high-efficient CO oxidation. Mater. Chem. Phys. 207, 11–22 (2018). https://doi.org/ 10.1016/j.matchemphys.2017.12.048
- L.H. Yao, W.Q. Cao, M.S. Cao et al., Doping effect on the adsorption of Na atom onto graphenes. Curr. Appl. Phys. 16, 574–580 (2016). https://doi.org/10.1016/j.cap.2016.03.001
- C. Marina, C. Simone, F.T. Gian et al., Structure and stability of hydrogenated carbon atom vacancies in graphene. Carbon 77, 165–174 (2014). https://doi.org/10.1016/j.carbon.2014.05.018
- K. Yamashita, M. Saito, T. Oda, Atomic geometry and stability of mono-, di-, and trivacancies in graphene. Jpn. J. Appl. Phys. 45, 6534–6536 (2006). https://doi.org/10.1143/JJAP.45.6534
- A.A. El-Barbary, R.H. Telling, C.P. Ewels et al., Structure and energetics of the vacancy in graphite. Phys. Rev. B 68, 144107 (2003). https://doi.org/10.1103/PhysRevB.68.144107
- A.V. Krasheninnikov, P.O. Lehtinen, A.S. Foster et al., Bending the rules: contrasting vacancy energetics and migration in graphite and carbon nanotubes. Chem. Phys. Lett. 418, 132–147 (2006). https://doi.org/10.1016/j.cplett.2005.10.106
- D.Q. Xia, C.L. Ren, W. Zhang et al., Theoretical study of the interaction between metallic fission products and defective graphite. Comput. Mater. Sci. 106, 129–134 (2015). https://doi.org/ 10.1016/j.commatsci.2015.04.029
- Y. Lei, A.S. Stephen, W.G. Zhu et al., Hydrogen-induced magnetization and tunable hydrogen storage in graphitic structures. Phys. Rev. B 77, 134114 (2008). https://doi.org/10.1103/Phys RevB.77.134114
- Q.G. Jiang, Z.M. Ao, W.T. Zheng et al., Enhanced hydrogen sensing properties of graphene by introducing a mono-atom-vacancy. Phys. Chem. Chem. Phys. 15, 21016–21022 (2013). https://doi.org/10.1039/c3cp52976b
- 55. G.K. Sunnardianto, I. Maruyama, K. Kusakabe, Dissociationchemisorption pathways of H2 molecule on graphene activated by a hydrogenated mono-vacancy V11. Adv. Sci. Eng. Med. 8, 421–426 (2016). https://doi.org/10.1166/asem.2016.1875

- G.K. Sunnardianto, I. Maruyama, K. Kusakabe, Storing-hydrogen processes on graphene activated by atomic-vacancies. Int. J. Hydrogen Energy 42, 23691–23697 (2017). https://doi.org/10.1016/ j.ijhydene.2017.01.115
- P. Hohenberg, W. Kohn, Inhomogeneous electron gas. Phys. Rev. B 136, 864 (1964). https://doi.org/10.1103/PhysRev.136.B864
- W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects. Phys. Rev. B 140, 1133 (1965). https://doi.org/10.1103/PhysRev.140.A1133
- G. Kresse, J. Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996). https://doi.org/10.1103/PhysRevB. 54.11169
- J.P. Perdew, J.A. Chevary, S.H. Vosko et al., Atoms, molecules, solids, and surfaces-applications of the generalized gradient approximation for exchange and correlation. Phys. Rev. B 46, 6671–6687 (1992). https://doi.org/10.1103/PhysRevB.46.6671
- P.E. Blochl, Projector Augmented-Wave Method. Phys. Rev. B 50, 17953–17979 (1994). https://doi.org/10.1103/PhysRevB.50. 17953
- G. Henkelman, B.P. Uberuaga, H. Jonsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths. J. Chem. Phys. **113**, 9901–9904 (2000). https://doi.org/10.1063/1.1329672
- G. Henkelman, H. Jonsson, Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. J. Chem. Phys. 113, 9978–9985 (2000). https:// doi.org/10.1063/1.1323224
- C. Li, C. Fang, C. Yang, First-principle studies of radioactive fission productions Cs/Sr/Ag/I adsorption on chrome-molybdenum steel in Chinese 200 MW HTR-PM. Nucl. Sci. Technol. 28, 79–88 (2017). https://doi.org/10.1007/s41365-017-0241-8
- V. Morón, P. Gamallo, R. Sayós, DFT and kinetics study of O/O₂ mixturesreacting over a graphite (0001) basal surface. Theor. Chem. Acc. **128**, 683–694 (2011). https://doi.org/10.1007/ s00214-010-0798-3
- 66. J. Fayos, Possible 3D carbon structures as progressive intermediates ingraphite to diamond phase transition. J. Solid State Chem. 148, 278–285 (1999). https://doi.org/10.1006/jssc.1999. 8448
- X.W. Sha, B. Jackson, First-principles study of the structural and energetic properties of H atoms on a graphite (0001) surface. Surf. Sci. 496, 318–330 (2002). https://doi.org/10.1016/S0039-6028(01)01602-8
- D.W. Boukhvalov, M.I. Katsnelson, A.I. Lichtenstein, Hydrogen on graphene: electronic structure, total energy, structural distortions and magnetism from first-principles calculations. Phys. Rev. B 77, 035427 (2008). https://doi.org/10.1103/PhysRevB.77.035427
- Y. Miura, H. Kasai, W. Dino et al., First principles studies for the disociative adsorption of H₂ on graphene. J. Appl. Phys. 93, 3395–3400 (2003). https://doi.org/10.1063/1.1555701
- P.O. Lethinen, A.S. Foster, Y. Ma et al., Irradiation induced magnetism in graphene: a density functional study. Phys. Rev. Lett. 93, 187202 (2004). https://doi.org/10.1103/PhysRevLett.93.187202
- O.V. Yazyev, L. Helm, Defect induced magnetism in graphene. Phys. Rev. B 75, 125408 (2007). https://doi.org/10.1103/Phys RevB.75.125408
- M.W.C. Dharma-Wardana, M.Z. Zgierski, Magnetism and structure at vacant lattice sites in graphene. Phys. E 41, 80–83 (2008). https://doi.org/10.1016/j.physe.2008.06.007
- X.Q. Dai, J.H. Zhao, M.H. Xie et al., First-principle study on magnetism induced by Vacanies in graphene. Eur. Phys. J. B 80, 343–351 (2011). https://doi.org/10.1140/epjb/e2011-10955-x
- 74. F. Banhart, J. Kotakoski, A.V. Krasheninnikov, Structural Defects in Graphene. ACS Nano 5, 26–41 (2011). https://doi.org/ 10.1021/nn102598m