Materials Research Express

PAPER

Hydrogen storage capacity on Li-decorated covalent organic framework-1: A first-principles study

Hui Zhao, Yurou Guan, Hailong Guo, Renjun Du and Cuixia Yan

Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming, 650093, People’s Republic of China

E-mail: 281613802@qq.com

Keywords: hydrogen storage, COF-1, Li-decorated, first-principles

Abstract

2D covalent organic framework-1 (COF-1) membrane is a potential hydrogen storage material. The hydrogen storage capacity of Li-decorated COF-1 has been studied by first-principles calculation. The results show its hydrogen storage capacity has been improved significantly by Li decoration, which is 7.69 wt%. Then ab initio molecular dynamics simulations at 300 K have been carried out and the results show that 12 H\textsubscript{2} molecules are stably absorbed on the double sides of COF-1 unit cell decorated by 6 Li atoms and the hydrogen storage capacity is 5.26 wt%.

1. Introduction

Nowadays, the contradiction between energy demand and environmental protection has become increasingly prominent, which promotes us to develop new clean energy to solve the pollution caused by fossil fuels. Among renewable energy, hydrogen is considered as an ideal energy carrier and a very promising substitute for fossil fuels due to its high energy-efficiency, environmental friendliness and abundance characteristics [1]. Now, hydrogen energy vehicles which use hydrogen as fuels [2] have being researched and developed very rapidly. The on-board storage of hydrogen in vehicles is crucial to promote the development of hydrogen energy vehicles. As a gas, hydrogen needs to be compressed under high pressure then is putted into a container which requires sophisticated tank systems due to the safety issues such as flammability and explosion [3].

So, the storage of hydrogen at ambient temperature and low pressure has been a research hotspot. Porous adsorbent (e.g., activated carbon, zeolite, and metal-organic frameworks (MOF)) are relatively ideal materials to store gas through weak van der Waals forces [4]. However, most existent adsorbents are unstable in humid environment (such as MOFs) and it is difficult to control their structures and customize the functionalities (such as activated carbon and zeolites) [5].

Yaghi and co-workers synthesized a new family of carbon-based crystalline porous material, which was named covalent organic frameworks (COFs) structure and can be divided into two-dimensional (2D) [6] and three-dimensional (3D) COFs [7] according to the dimension of their composition unit. COFs are composed of light weight elements (B, C, N, O, H) that are bonded with each other by strong covalent bonds, which makes COFs low density and stable. In addition, similar to other carbon-based materials, COFs are porous and ordered. Due to the above advantages, COFs are suitable for hydrogen adsorption and have been researched for hydrogen storage theoretically and experimentally.

COFs (2D and 3D) present excellent potential on hydrogen storage. The hydrogen storage capacity of COF-5 (2D) is 3.4 wt% at 50 bar and 77 K [8]. 3D COFs have higher hydrogen capacity compared to 2D COFs due to their larger pore volume. Yaghi et al found the hydrogen uptake capacity of COF-102 is 7.16 wt% at 77 K and 35 bar and COF-102 has 9.95 wt% hydrogen capacity at 77 K and 100 bar [9, 10]. Then George et al have designed some new 3D COFs for hydrogen storage and found among these COFs the hydrogen capacity of COF-102-3 can be up to 26.7 wt% under 100 bar at 77 K and 6.5 wt% at 300 K [11]. Though 2D COFs show a lower
hydrogen storage capacity compared to 3D COFs, 2D COFs have better thermal stability and are easier to be synthesized, indicating 2D COFs are more appropriate to store hydrogen [12].

Although COFs (2D and 3D) present excellent hydrogen storage capacity under high pressure, their hydrogen storage capacities are very terrible and much lower than the standard published by United States Department of Energy (DOE) that the capacity of material achieves 4.5 wt% at a temperature range of 233–333 K by the year 2020 [12, 13]. The poor hydrogen storage performance of COFs at room temperature and atmospheric pressure attributed to a weak binding energy between hydrogen and COF, which is far below the optimal binding energy of hydrogen, $-0.2 \text{ eV} \text{ to } -0.4 \text{ eV}$ [14]. It is reported that the hydrogen adsorption ability of COFs decorated by metal atoms have been improved significantly [10, 15–18]. Moreover, the Lithium atom is an excellent dopant to strengthen the interaction between hydrogen and COFs [10, 17–19]. COF-1 is a typical 2D COF structure with the highest adsorption heat synthesized by Côté et al [6] and its membrane can be fabricated using exfoliated microporous COF-1 nanosheets [20], indicating that COF-1 is a promising material for hydrogen storage [8]. The hydrogen storage capacity of COF-1 is 1.28 wt% at 77 K and 1 atm but is 0.26 wt% at room temperature and 100 bar, which is very poor [21].

In this paper, the hydrogen storage properties of COF-1 decorated by Li atom (Li-COF-1) have been investigated by first-principles calculation. Firstly, the optimal adsorption sites of Li atom on COF-1 have been identified. And then the adsorption energies and mechanism of H$_2$ molecules absorbed on Li-COF-1 have been studied. Finally, ab initio molecular dynamics (MD) simulations are carried out to explore the stability of hydrogen adsorption system at room temperature.

2. Computational details

The calculations are performed by the CASTEP code of material studio 8.0 [22] with the ultrasoft pseudopotentials. We use the generalized gradient approximation (GGA) [23] with the Perdew–Burke–Ernzerhof (PBE) [24] to describe exchange-correlation interaction between the electrons. Previous studies show that GGA would underestimate the relatively weak binding energy of H$_2$ molecules on substrate [25, 26]. The long-range dispersion correction (DFT-D) within the Grimme scheme is used through all calculations to describe the weak interaction between the H$_2$ and the substrate [27]. Previous investigations of hydrogen storage prove that GGA with dispersion corrections per Grimme could give a good description of this van der Waals interaction [28–30]. Considering the calculation cost and the accuracy of results, the cutoff energy for the plane-wave basis set is set to 500 eV and a (6 × 6 × 1) mesh of k-points is used for the COF-1 cell. The vacuum is set to 20 Å along the c direction to avoid the interaction between the periodic layers. The lattice and atoms are allowed to be fully relaxed on the process of geometry optimization until the force is smaller than 0.05 eV Å$^{-1}$ and the energy tolerances less than 2.0 × 10$^{-5}$ eV per atom. The self-consistent field (SCF) convergence threshold is 1.0 × 10$^{-6}$ eV/atom. In addition, because the COF-1 decorated by one Li atom is an open-shell structure with odd electrons, spin-unrestricted calculations are performed [31].

The binding energy is a crucial factor to judge the hydrogen capacity. The binding energy of Li atom to the COF-1 can be defined in the following,

$$E_b = \left[ E_{\text{COF-1} + nLi} - \left( E_{\text{COF-1}} + nE_{Li} \right) \right] / n$$ (1)

Where $E_b$ is the average binding energy of each Li atom absorbed on COF-1 structure, $E_{\text{COF-1} + nLi}$, $E_{\text{COF-1}}$, and $nE_{Li}$ are the total energy of COF-1 structure with n Li atoms adsorbed, COF-1 structure and n Li atom, respectively.

The adsorption energy and average adsorption energy of H$_2$ molecules absorbed on COF-1 decorated by Li single side can be defined as follows:

$$E_{ad} = E_{nH2 + Li + COF-1} - E_{(n-1)H2 + Li + COF-1} - E_{LiH2}$$ (2)

$$\bar{E}_{ad} = \left( E_{nH2 + Li + COF-1} - E_{Li + COF-1} - nE_{H2} \right) / n$$ (3)

Where $E_{nH2 + Li + COF-1}$, $E_{(n-1)H2 + Li + COF-1}$, $E_{Li + COF-1}$, $E_{H2}$ denote the total energy of Li-COF-1 with n H$_2$ molecules absorbed, Li-COF-1 with (n-1) H$_2$ adsorbed, Li-COF-1 system and free H$_2$ molecule, respectively.

3. Results and discussions

3.1. COF-1 and Li-COF-1 structures

Figure 1 shows the optimized structure of COF-1 unit cell. The lattice constants of COF-1 structure are $a = b = 15.11 \text{ Å}$, and the bond lengths of C-B, B-O are 1.55 Å and 1.39 Å, respectively, which is consistent well with the constants from Ahuja’s work [32]. Like porous graphene, there are two kinds of carbon atoms in COF-1 unit cell, which are named C1 and C2, respectively. C1 atom is connected with two carbon atoms and one hydrogen atom. And C2 atom is connected with two carbon atoms and one B atom. The twelve high symmetry
adsorption sites of Li atom adsorbed on the single side of COF-1 are considered. H1, H2, H3 and H4 are the centers of boron-oxygen ring, the pore between the boron-oxygen ring and the C hexagon ring, C hexagon ring and the big hole, respectively. B1, B2, B3 and B4 are the bridge sites over C2-B bond, B-O bond, C1-C2 bond and C1-C1 bond, respectively. T1, T2, T3 and T4 are top sites directly above B atom, O atom, C2 atom, and C1 atom, respectively. The high symmetry adsorption sites are shown in figure 1. As a reference, the adsorption of hydrogen molecule on COF-1 layer has been investigated and found that the adsorption energy is $-0.048$ eV, which indicates the weak interaction between hydrogen molecule and COF-1 layer.

The site H3 is energetically favorable for Li atom and the binding energy is 1.765 eV (seen table S1 is available online at stacks.iop.org/MRX/7/035506/mmedia), which is higher than the cohesive energy of Li metal bulk (1.63 eV), as shown in figure 2(a). The Mulliken atomic populations show that Li atom loses the charge of 1.13 e and COF-1 gets the charge, which indicates a charge transfer between Li atom and COF-1 layer. Hence, the electron potential difference between the positively charged Li and negatively charged C atoms causes an electronic field. The deformation density map of Li-COF-1 has been calculated to analyze the charge distribution, as shown in figure 2(b). It is observed that no electron accumulates between the Li atom and COF-1, indicating that the delocalized electrons transfer from Li atom to COF-1 layer and a weak charge back-donation from COF-1 layer to the Li atom, which is similar to the previous results [33].
To furtherly understand the interaction between the Li atom and COF-1 layer, the local density of states of Li atom and the C hexagon ring around Li atom in the Li-COF-1 system have been calculated, as shown in figure 3. It is observed that the 2 s orbital of Li atom is unoccupied and is considered that the electron in 2 s orbital of Li atom transfers to C 2p orbital due to the interaction between Li and COF-1 layer, which is consistent with the above ones. An almost complete overlapping between 2 s orbital of Li atom and 2p orbital of C atoms near Fermi energy can be seen, which indicates the strong hybridization between the Li atom and COF-1. All the results show that Li atom can be stably adsorbed on COF-1 layer.

Next, the situations of two Li atoms absorbed bilaterally on COF-1 are studied because positively charged Li atoms could act as active sites for H2 adsorption to increase the available adsorption surface area for H2 molecules. After relaxation, the stable sites of two Li atoms on COF-1 are shown in figure 4(a), in which one Li atom is still adsorbed on H3 site and the other one also occupies the center of the C hexagon ring. The two Li atoms both lose the charges and the average binding energy is 1.818 eV, also higher than the cohesive energy of Li metal bulk. Then the coverage degree of Li atoms on COF-1 layer is increased to further improve the hydrogen storage capacity of Li-COF-1 system. Considering the most concentration of Li atoms and space steric of hydrogen molecules, one stable structure of six Li atoms absorbed on Li-COF-1 is provided, as shown in figure 4(b). The six Li atoms all occupy the hole sites of C hexagon rings and a slight deformation can be observed. The average binding energy of Li atoms on COF-1 is 1.70 eV, which is higher than the cohesive energy of Li metal bulk. Therefore, Li atoms can be uniformly dispersed on COF-1.

3.2. Adsorption of H2 molecules on Li-COF-1 layers
The hydrogen storage of COF-1 single-side decorated by Li atoms is investigated here. The optimized geometries of H2 molecules absorbed on Li-COF-1 are shown in figure 5. The adsorption energy, the average adsorption energy, the bond characteristics of H2 molecules, the distance between H2 molecules and Li atom, and charge of Li atom are summarized in table 1. The first H2 molecule is above the Li atom and is parallel to the Li-COF-1 layer with the adsorption energy of −0.263 eV, as shown in figure 5(a). When the second H2 molecule is adsorbed, the two H2 molecules are both above the C atom and adsorbed around Li atom symmetrically, as shown in figure 5(b). Meantime, the two H2 molecules are also parallel to Li-COF-1 layer with the average adsorption energy of −0.228 eV. However, the adsorption energy of the third H2 molecule is −0.239 eV, whose absolute value is higher than that of the second H2 molecule. Figure 5(d) shows the structure of 4 H2 molecules absorbed on Li-COF-1. It is obviously observed that the distance between the Li atom and the fourth H2 molecule is longer than the distances between Li and three other H2 molecules. It causes the adsorption energy to be only −0.043 eV (see table 1), which is higher than the ideal one (−0.2 eV to −0.4 eV). Therefore, the adsorption of the fourth H2 molecule is weak. From figure S2, no overlap of electronic cloud between the fourth H2 molecules and Li or COF-1 can be observed, which also proves the weak adsorption of the fourth H2 molecule on Li-COF-1. It is considered that 3 H2 molecules can be adsorbed on per Li atom based on the above results. From table 1, it is observed that the bond lengths of the H2 molecules of all four geometries are ranging from 0.757 Å to 0.760 Å, which is slightly longer than that of free H2 molecule of 0.753 Å (that is consistent with the result in reference [34]). It indicates that H2 molecules are all adsorbed in the non-dissociative form.

Figure 3. Local density of state of Li atom and C hexagon ring around Li atom in the Li-COF-1.
To explore the mechanism of H\textsubscript{2} molecule adsorbed on the Li-COF-1 system, the partial density of state (PDOS) of the Li-COF-1 adsorbed H\textsubscript{2} molecule are calculated and shown in figure 6. When the first H\textsubscript{2} molecule is adsorbed on Li-COF-1, a sharp peak of H\textsubscript{2} is observed about $-10$ eV which is caused by the $\sigma$ orbital of H\textsubscript{2} molecule [33, 35, 36]. For the all situation of nH\textsubscript{2} (n = 1, 2, 3, respectively) molecules adsorbed on Li-COF-1, the overlap between Li 2 s orbital and H 1 s orbital can be observed in the range of 1 eV to 3 eV. It is considered that the adsorption of hydrogen on Li-COF-1 is not bonded through the Kubas type interaction [37] but by the weak electrostatic interaction between the Li cation and the induced H\textsubscript{2} dipole. By analyzing the Mulliken population, it is found that every H\textsubscript{2} molecule has a slight negative charge and Li atom is more positive than that of Li atom.
without H\textsubscript{2} molecules adsorption, indicating that the charge transfer occurs from Li atom to H\textsubscript{2} molecules and the H\textsubscript{2} molecules are polarized. In addition, it is observed that the \(\sigma\) orbital of H\textsubscript{2} molecule far from Fermi level shifts towards right and splits into several peaks as the increasing number of adsorbed H\textsubscript{2} molecules. It indicates that with the increase of the adsorbed H\textsubscript{2} molecules the interaction between H\textsubscript{2} molecule and Li-COF-1 becomes weaker and also reflects that the strong interaction between H\textsubscript{2} molecules which affect the adsorption energy of H\textsubscript{2} molecules. In the meantime, the average distance between three H\textsubscript{2} molecules adsorbed on Li-COF-1 is shorter than that of two H\textsubscript{2} molecules adsorbed on Li-COF-1. Therefore, it is considered that the H\textsubscript{2}-H\textsubscript{2} interaction makes the adsorption energy of the third molecule increased.

Then the case of COF-1 layer decorated bilaterally by Li atoms has been investigated. Figure 7 shows the optimized configurations of H\textsubscript{2} molecules are adsorbed on COF-1 layer decorated bilaterally by Li atoms. From the side views in figure 7, it is obviously observed that H\textsubscript{2} molecules are absorbed around the Li atoms. As shown in table 2, similar to the situation of H\textsubscript{2} molecules adsorbed on Li-COF-1 unilaterally, the fourth H\textsubscript{2} molecule is adsorbed and the adsorption energy is just \(-0.117\) eV, which is much higher than the ideal one. Therefore, it is considered that the H\textsubscript{2} interaction makes the adsorption energy of the third molecule increased.

Table 1. The average adsorption energy \(E_{\text{ad}}\) and adsorption energy \(E_{\text{ad}}\) of H\textsubscript{2} molecules on the single side of Li-COF-1. \(d_{\text{H}}(\text{Å})\) is the average bond length of H\textsubscript{2} molecules. \(d_{\text{Li-C}}(\text{Å})\) is the average distance between Li atom and H\textsubscript{2} molecules, \(Q_{t}\) is the charge of Li atom.

| Number of H\textsubscript{2} | 1      | 2      | 3      | 4      |
|-----------------------------|--------|--------|--------|--------|
| \(E_{\text{ad}}(\text{eV})\) | -0.263 | -0.193 | -0.239 | -0.043 |
| \(\bar{E}_{\text{ad}}(\text{eV})\) | -0.263 | -0.228 | -0.231 | —      |
| \(d_{\text{H}}(\text{Å})\)   | 0.758  | 0.757  | 0.760  | —      |
| \(d_{\text{Li-H}}(\text{Å})\) | 1.958  | 2.000  | 2.02   | 2.296  |
| \(Q_{t}\)                   | 1.31   | 1.41   | 1.55   | —      |

Figure 6. The PDOS of Li \(s\) (red curve) and H\textsubscript{2} \(s\) orbital (black curve) orbitals for 1-3 H\textsubscript{2} molecules adsorbed on Li-COF-1 layer.

To test the stability of hydrogen molecules on the Li atoms decorated COF-1 system at ambient temperature, \textit{ab initio} MD as implemented in CASTEP simulations have been carried out. NVT (N, V and T are the constant number of atoms, constant volume and constant temperature, respectively) ensemble is selected and Nose-Hoover thermostat method is used to control the temperature at 300 K in the calculation. The simulation time step is set 1 fs and the total simulation time is 1.5 ps to enable the calculation finish within a reasonable time range, which are consistent with the parameters from the references [33, 35]. As shown in figure 8, Li atoms are adsorbed on COF-1 layer uniformly and stably and one H\textsubscript{2} molecule escapes from each Li atom, which indicates that every Li atom can adsorb three H\textsubscript{2} molecules stably at room temperature. So 12 H\textsubscript{2} molecules can be adsorbed on Li-COF-1 system with the gravimetric hydrogen storage capacity of 5.26 wt\% at room temperature.
4. Conclusions

In summary, the hydrogen storage properties of the Li-COF-1 system have been studied based on the first principles calculation. The results show that 6 Li atoms can disperse uniformly on COF-1 layer bilaterally and 3 \( \text{H}_2 \) molecules can be adsorbed stably around per Li atom in the system Li-COF-1. The hydrogen capacity is 7.69 wt%. Under the condition of 300 K, the results from \textit{ab initio} MD simulations show that 12 \( \text{H}_2 \) molecule can be adsorbed stably on the Li-COF-1 layer and the hydrogen storage capacity is 5.26 wt%, which is higher than standard of DOE (4.5 wt%). These results indicate that Li-COF-1 is a potential hydrogen storage material at ambient condition.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (11564022, 11674136), the Thousand Talents Plan-The Recruitment Program for Young Professionals (1097816002), Yunnan Province for Recruiting High-Caliber Technological Talents (1097816002).

Declaration of interests

The authors declared that there is no conflict of interest.
References

[1] Sherif S A, Barbir F and Veziroglu T N 2005 Wind energy and the hydrogen economy—review of the technology Sol. Energy 78 647–60
[2] Bucior B J et al 2019 Energy-based descriptors to rapidly predict hydrogen storage in metal–organic frameworks Molecular Systems Design & Engineering. 4 162–74
[3] Ao Z, Dou S, Xu Z, Jiang Q and Wang G 2014 Hydrogen storage in porous graphene with Al decoration Int. J. Hydrogen Energy 39 16244–51
[4] Keskin S, van Heest T M and Sholl D S 2010 Can metal–organic framework materials play a useful role in large-scale carbon dioxide separations? Chem. Sus. Chem. 3 879–91
[5] Li Z et al 2015 An azine-linked covalent organic framework: synthesis, characterization and efficient gas storage Chemistry—A European Journal. 21 12079–84
[6] Côté A P, Benin A I, Ockwig N W, ‘Keeffe M, Matzger A J and Yaghi O M 2005 Porous, crystalline, covalent organic frameworks Science 310 1166–70
[7] El-Kaderi H M et al 2007 Designed synthesis of 3D covalent organic frameworks Science 316 268–72
[8] Han S S, Furukawa H, Yaghi O M and Goddard W A 2008 Covalent organic frameworks as exceptional hydrogen storage materials JACS 130 11580–1
[9] Furukawa H and Yaghi O M 2009 Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy applications JACS 131 8875–83
[10] Xia L and Liu Q 2016 Lithium doping on covalent organic framework-320 for enhancing hydrogen storage at ambient temperature J. Solid State Chem. 244 1–5
[11] Klontzas E, Tylankanis E and Froudakis G E 2010 Designing 3D COFs with enhanced hydrogen storage capacity Nano Lett. 10 452–4
[12] Ghosh S and Singh J K 2019 Hydrogen adsorption in pyridine bridged porphyrin–covalent organic framework Int. J. Hydrogen Energy 44 1782–96
[13] Stetson N T 2015 Hydrogen storage program area—plenary presentation Annual Merit Review and peer Evaluation Meeting, Fuel Cell Technologies Office. (US Department of Energy) 2015
[14] Lochan R C and Head-Gordon M 2006 Computational studies of molecular hydrogen binding affinities: The role of dispersion forces, electrostatics, and orbital interactions Phys. Chem. Chem. Phys. 8 1357–70
[15] Ganz E and Dornfeld M 2012 Storage capacity of metal–organic and covalent–organic frameworks by hydrogen spillover The Journal of Physical Chemistry C 116 3661–6
[16] Yang Z and Cao D 2012 Effect of Li doping on diffusion and separation of hydrogen and methane in covalent organic frameworks The Journal of Physical Chemistry C 116 12591–8
[17] Srepusharawoot P, Swatsitang E, Amornkitbamrung V, Pinsook U and Ahuja R 2013 Hydrogen adsorption of Li functionalized covalent organic framework-366: an ab initio study Int. J. Hydrogen Energy 38 14276–80.

[18] Ke Z, Cheng Y, Yang S, Li F and Ding L 2017 Modification of COF-108 via impregnation/functionlization and Li-doping for hydrogen storage at ambient temperature Int. J. Hydrogen Energy 42 11461–8

[19] Dimitrakakis G K, Tylianakis E and Froudakis G E 2008 Pillared graphene: a new 3D network nanostructure for enhanced hydrogen storage Nano Lett. 8 3166–70

[20] Li G, Zhang K and Tsuru T 2017 Two-dimensional covalent organic framework (COF) membranes fabricated via the assembly of exfoliated COF nanosheets ACS Applied Materials & Interfaces 9 8433–6

[21] Li Y and Yang R T 2008 Hydrogen storage in metal-organic and covalent-organic frameworks by spillover AlChE J. 54 269–79

[22] Segall M D et al 2002 First-principles simulation: ideas, illustrations and the CASTEP code J. Phys. Condens. Matter 14 2717–44

[23] Perdew J P et al 1992 Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation Physical Review B 46 6671

[24] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865

[25] Zhou Y, Chu W, Jing F, Zheng J, Sun W and Xue Y 2017 Enhanced hydrogen storage on Li-doped defective graphene with B substitution: a DFT study Appl. Surf. Sci. 410 166–76

[26] Kim Y H, Zhao Y, Williamson A, Heben M J and Zhang S B 2006 Nondissociative adsorption of H2 molecules in light-element–doped fullerences Phys. Rev. Lett. 96 016102

[27] Grimme S 2006 Semiempirical GGA-type density functional constructed with a long-range dispersion correction J. Comput. Chem. 27 1787–99

[28] Tan X, Tahini H A and Smith S C 2016 Conductive boron-doped graphene as an ideal material for electrocatalytically switchable and high-capacity hydrogen storage ACS Applied Materials & Interfaces 8 32815–22

[29] Si L and Tang C 2017 The reversible hydrogen storage abilities of metal Na (Li, K, Ca, Mg, Sc, Ti, Y) decorated all-boron cage B28 Int. J. Hydrogen Energy 42 16611–9

[30] Zhang X, Tang C and Jiang Q 2017 Electric field induced enhancement of hydrogen storage capacity for Li atom decorated graphene with Stone-Wales defects Int. J. Hydrogen Energy 41 10776–85

[31] Wang L, Chen X, Du H, Yuan Y, Qi H and Zou M 2018 First-principles investigation on hydrogen storage performance of Li, Na and K decorated borophene Appl. Surf. Sci. 427 1030–7

[32] Srepusharawoot P, Scheicher R H, Moysés Araújo C, Blomqvist A, Pinsook U and Ahuja R 2009 Ab initio study of molecular hydrogen adsorption in covalent organic framework-1 The Journal of Physical Chemistry C 113 8498–504

[33] Wang F et al 2017 Li-decorated porous graphene as a high-performance hydrogen storage material: A first-principles study Int. J. Hydrogen Energy 42 10099–108

[34] Reunchan P and Jhi S-H 2011 Metal-dispersed porous graphene for hydrogen storage Appl. Phys. Lett. 98 093103

[35] Yuan L et al 2019 First-principles study of V–decorated porous graphene for hydrogen storage Chem. Phys. Lett. 726 57–61

[36] Yuan L et al 2018 Hydrogen storage capacity on Ti-decorated porous graphene: first-principles investigation Appl. Surf. Sci. 434 843–9

[37] Kubas G J 2001 Metal–dihydrogen and σ bond coordination: the consummate extension of the Dewar–Chatt–Duncanson model for metal–olefin π bonding J. Organomet. Chem. 635 37–68