First-principles study on methane storage properties of porous graphene modified with Mn

Qiuyu Zhao¹ · Yingjie Zhao¹ · Yuhong Chen¹,² · Jiaming Ju¹ · Wenhui Xu¹ · Meiling Zhang¹ · Cuicui Sang¹ · Cairong Zhang¹,²

Received: 5 July 2021 / Accepted: 21 October 2021 / Published online: 19 November 2021
© The Author(s), under exclusive licence to Springer-Verlag GmbH, DE part of Springer Nature 2021

Abstract
Porous graphene (PG) has a promising future for gas storage owing to its unique pore characteristics and large specific surface area. The adsorption properties of PG and Mn atoms decorated PG (Mn-PG) for methane (CH₄) molecules have been studied based on the first-principles density functional theory. It is discovered that the optimum adsorption position of CH₄ on PG is the carbon ring pore, and the adsorption energy is −0.174 eV. The optimal position of the PG system decorated by single Mn atom is the central hole of the carbon ring, and the optimal position of the two Mn atoms is that Mn atoms are, respectively, located at different carbon ring holes on the opposite side of PG, with an average binding energy of −4.101 eV. The modification of the Mn atom enhances the electronegativity of the PG substrate and forms a negative electrical center at the carbon ring, which facilitates the enhancement of the adsorption performance of the CH₄ molecules that are positively charged with the surface. The CH₄ molecule, close to Mn atom shows negative charge, and its strong electrostatic interaction with positively charged Mn atom is dominant, resulting in higher adsorption energy. The surface of CH₄ molecule far away from the Mn atom is positively charged, the weak electrostatic interaction with the negatively charged PG substrate and the Van der Waals interaction between CH₄ molecules are dominant, and the adsorption energy is low. The CH₄ molecules are adsorbed on the PG surface through the electrostatic interaction with Mn atoms and PG substrate as well as the intermolecular force of CH₄ molecules. The Mn-PG system is single-sided adsorption 6 CH₄ molecules, and the average adsorption energy is −0.345 eV. When two Mn atom modification PG, 12 CH₄ molecules can be adsorbed on both sides, and the average adsorption energy is −0.338 eV, the adsorption capacity is up to 38.43 wt.%.

Keywords Porous graphene · Mn modified · Methane · First principles

1 Introduction

With the development of science and technology, people have been exploring the earth deeply; at the same time, it also brings various problems such as energy depletion and environmental pollution. The combustion of coal, oil, and other fossil fuels will produce CO₂ and a large number of harmful gases [1]. The main component of natural gas is methane (CH₄) [2]. Compared with other fossil fuels, CH₄ combustion produces less CO₂, and the energy produced by a CH₄ molecule is 3.1 times that of a hydrogen (H₂) molecule. Natural gas resources are rich globally, and it is an important transition fuel to achieve low-carbon energy [3]. In addition, CH₄ is a greenhouse gas, escaping into the atmosphere will aggravate the greenhouse effect, accounting for about 20% of global warming [4]. The adsorption and storage of CH₄ gas is a hot topic in scientific research, which is an effective means to solve the greenhouse effect and low-carbon alternative energy. Therefore, it is necessary to seek a kind of efficient, safe, and large storage capacity of CH₄ storage materials. CH₄ storage materials are usually characterized by porous structures, such as zeolite [5], molecular sieves [6], activated carbon [7], covalent organic framework materials.
(COFs) [8], metal–organic framework materials (MOFs) [9, 10] are common gas storage materials. The storage capacity of CH₄ is an obvious linear relationship with the surface area of the molecular sieve and other materials, the larger the surface area, the more adsorption capacity, but the upper limit is low [11]. COFs, MOFs porous material surface area, aperture, pore volume have an important impact on the gas storage capacity of CH₄ [12]. Studies have shown a new synthetic COFs material (COP-150) at 273 K, 100–5 bar cycle pressure of CH₄ working capacity reached 0.625 g/g (294 cm³stp/cm³), and the flexibility of the material provides fast desorption of CH₄, and hydrophobicity and the nature of the covalently bonded framework allows the material to tolerate harsh conditions [13]. MOFs materials have also achieved much progress as one of the best materials for CH₄ storage performance. The CH₄ adsorption capacity of various MOFs can reach 236–263 cm³stp/cm³, under the circulating pressure of 298 K and 100–5 bar [14–16], higher pressure can increase the adsorption capacity of CH₄ to 324 cm³stp/cm³ (298 K, 250 bar) [17]. However, whether the CH₄ working capacity can reach the storage target of the U.S. Department of Energy (DOE) (0.5 g/g (low pressure) and 350 cm³stp/cm³ (65–5 bar) are more important in practical applications, currently CH₄ working capacity is 200–208 cm³stp/cm³ at 298 K and 80–5 bar, which still does not meet the standard of the U.S. DOE [14, 16, 18]. Increased pressure such as Nu-1501-Al (270 K, 100–5 bar) working capacity reached 0.60 g/g (238 cm³stp/cm³) [15], and ST-2 at 298 K, 200–5 bar working capacity is 0.567 g/g (289 cm³stp/cm³) [17]. Although the weight storage capacity of some new materials had reached (0.5 g/g) the target, the volume capacity is still not achieved, or a large amount of storage is implemented under high-pressure conditions, the actual application still remain difficult.

Graphene is a two-dimensional material, and its unique nanostructure gives it excellent thermal conductivity [19], mechanical [20], optical [21], and electrical properties [22]. It is a strong competitor in the fields of sensors, composites, and energy storage [23], as well as a potential medium for CH₄ storage. The adsorption energy of CH₄ on graphene increases as the number of graphene layers increases, with a maximum of −0.267 eV [24], indicating that the adsorption of CH₄ on intrinsic graphene is weak. Regulating the electronic structure of graphene through defects, doping or metal element modification can improve the adsorption performance of gas [25–27]. Calculations show that the adsorption energy of Ag modified graphene can reach −0.399 eV in the presence of ambient O₂ [28], and that of Pt-modified graphene can reach −0.485 eV [29], which is much higher than that on intrinsic graphene. Compared with intrinsic graphene, CH₄ has higher adsorption energy, more charge transfer, smaller adsorption distance, and stronger interaction on metal-modified graphene. However, owing to the small pore defects of graphene structure and limited adsorption space, the overall adsorption capacity is low.

Porous graphene is a two-dimensional structure derived from graphene. There are nanopores with adjustable size and shape on the structure, and it has a porous structure which is a common feature of energy storage materials. It has been revealed that porous graphene with different geometrical configurations will exhibit different properties of semiconductor, semi-metal, or metal [30]. The existence of defects makes it have a larger specific surface area and more active sites compared with intrinsic graphene, which creates good conditions for gas adsorption and storage [31–33]. Bieri et al. [34] successfully prepared a porous graphene (PG) composed of two C₆H₃ rings through experiments, with the pore spacing of 7.400 Å. The mass of the porous graphene in the same size crystal cell is about two-thirds that of the intrinsic graphene, and it has a larger specific surface area, showing good gas adsorption performance. H₂ storage performance of PG modified with transition metal shows that H₂ is physically adsorbed on the substrate surface in molecular form. The main mechanism is coulomb interaction between H₂ and metal atoms and Van der Waals interaction between the polarization charge of H₂ and PG. The average adsorption energy is −0.2 to −0.6 eV/CH₄, and the adsorption capacity can reach 9.09 wt.% [35, 36], which is higher than the U.S. DOE technical targets for onboard hydrogen storage for light-duty vehicles [37, 38], so we chose PG as the substrate to study the adsorption properties of CH₄. The adsorption performance of CH₄ was tested by studying the graphene and graphdiyne modified by alkali metals, alkaline earth metals, and transition metals. The results showed that the adsorption energy of CH₄ was larger (−0.861 eV, −0.751 eV) when Mn-modified intrinsic graphene (Mn-GR) and N-doped graphdiyne (Mn-N-GDY), and the adsorption capacity was greatly improved, meanwhile, the geometric structure of the base remains stable [39, 40]. The adsorption capacity of 2Mn-GN can reach 32.93 wt.%, which is far behind the storage target of U.S. DOE [39]. To improve CH₄ adsorption capacity, this paper studied the CH₄ adsorption performance of PG structure and Mn-modified PG structure (Mn-PG), hoping to provide theoretical support for the research and development of safe and efficient CH₄ storage.

2 Calculation methods and models

The calculation used in this study employs the CASTEP module under Material Studio 8.0 software [41], based on the first-principles pseudopotential plane-wave method considering density functional theory. The Perdew-Burke-Ernzerhof (PBE) exchange–correlation functional in the generalized
gradient approximation (GGA) form was selected [42], and
the super-soft pseudopotential was determined to describe
the interaction between electrons and ions. Because the GGA
functional may underestimate the weak adsorption energy of
CH₄ molecules on the PG surface, the Van der Waals correction
(DFT-D method) was used in the calculation [43]. All the
atoms in the calculation were completely relaxed, and the con-
vergence criterion of structure optimization was that the force
of each atom was less than 0.03 eV/Å, the energy difference
was less than 1.0 × 10⁻⁶ eV/atom, and the self-consistent field
convergence threshold was 1.0 × 10⁻⁶ eV/atom. By testing the
cut-off energy and K-point sampling of the system, consider-
ing the calculation accuracy and calculation cost, the cut-off
energy was selected as 400 eV, and the K-point sampling in the
Brillouin zone was 5 × 5 × 1. The calculation of the porous gra-
phene crystal cell satisfies the periodic boundary conditions,
and the vacuum layer was 25 Å to avoid interlayer interaction.

The binding energy ($E_b$) and average binding energy ($\overline{E_b}$) of the Mn atom on PG are defined as follows, respectively:

$$E_b = E_{n\text{Mn} + \text{PG}} - E_{(n-1)\text{Mn} + \text{PG}} - E_{\text{Mn}}$$  (1)

$$\overline{E_b} = (E_{n\text{Mn} + \text{PG}} - E_{\text{PG}} - nE_{\text{Mn}})/n$$  (2)

where $E_{n\text{Mn} + \text{PG}}$ and $E_{(n-1)\text{Mn} + \text{PG}}$, respectively, represent the total energy of PG modified by $n$ and $(n-1)$ Mn atoms, $E_{\text{PG}}$ is the total energy of PG, and $E_{\text{Mn}}$ is the energy of a free Mn atom.

The continuous adsorption energy ($E_{ad}$) and average adsorption energy ($\overline{E_{ad}}$) of the CH₄ molecule are defined as follows:

$$E_{ad} = E_{i\text{CH}_4+n\text{Mn} + \text{PG}} - E_{(i-1)\text{CH}_4+n\text{Mn} + \text{PG}} - E_{\text{CH}_4}$$  (3)

$$\overline{E_{ad}} = (E_{i\text{CH}_4+n\text{Mn} + \text{PG}} - E_{(i-1)\text{CH}_4+n\text{Mn} + \text{PG}} - iE_{\text{CH}_4})/i$$  (4)

where $E_{i\text{CH}_4+n\text{Mn} + \text{PG}}$ and $E_{(i-1)\text{CH}_4+n\text{Mn} + \text{PG}}$, respectively, represent the total energy of $n$ Mn-PG system with $i$ and $i-1$ CH₄ molecules, and $E_{\text{CH}_4}$ is the energy of a free CH₄ molecule.

In the Mn-modified PG structure, the calculation formula of stored CH₄ mass fraction (CH₄ molecule adsorp-
tion capacity) is defined as follows:

$$\text{CH}_4(\text{wt.}%)= \left[ \frac{m_{\text{CH}_4}}{m_{\text{CH}_4} + m_{n\text{Mn} + \text{PG}}} \right] \times 100$$  (5)

where $m_{\text{CH}_4}$ and $m_{n\text{Mn} + \text{PG}}$, respectively, represent the mass of CH₄ molecules and the PG system modified by $n$ Mn atoms.

According to the experimental results, the PG structure is formed by two C₆H₃ rings connected, or it can be seen as formed by H atoms saturated suspension bonds after removing part of C atoms in 3 × 3 graphene supercells. The optimized geometry of the PG primitive cell is shown in Fig. 1a, and the lattice constant is 7.480 Å, which is in good agreement with the experimental value of 7.400 Å [34]. The length of C₆H₃–C₆H₃ bond of carbon hexagonal ring is 1.400 Å; the length of C₆H₃–C₆H₃ bond connecting two carbon hexagonal rings is 1.492 Å, and the length of C–H bond is 1.084 Å. The calculated direct bandgap of PG is 2.398 eV, which is consistent with 2.400 eV calculated by VASP software [44], indicating that the calculation model adopted in this paper is correct, the calculation method and calculation accuracy are reasonable, and the calculation results are reliable.

---

**Fig. 1** a Top view of the geometry of PG unit cells. b–c Top and side views of two stable geometric structures of PG system modified by Mn atom (gray, white, and purple spheres represent C, H, and Mn atoms, respectively)
3 Results and discussion

3.1 Adsorption properties of CH$_4$ molecules on porous graphene

In the porous graphene system, six symmetric adsorption sites as shown in Fig. 1a are considered: 1 is the carbon ring hole; 2 is the bridge between the two carbon rings; 3 is the carbon-hydrogen ring hole, and 4 is the center of the carbon-hydrogen macrocycle; 5 is the C top of the carbon ring; 6 is the C–C bridge in the carbon ring. After placing CH$_4$ molecules in the above six initial positions for geometric structure optimization, the optimal adsorption position of CH$_4$ molecules on the porous graphene system was explored by calculating the adsorption energy. It is discovered that the best adsorption position of single CH$_4$ molecule on the porous graphene system is the top position of position 1, as shown in Fig. 2, where the adsorption energy is $-0.174$ eV, and the distance between CH$_4$ molecule and PG substrate is 3.353 Å. This is similar to the optimal adsorption position of CH$_4$ in the intrinsic graphene structure, which is the central hole of carbon ring [39]. The adsorption energy of CH$_4$ molecule in PG system is lower, but it has more adsorption sites than that in intrinsic graphene system. Therefore, based on the research of Mn atom modified intrinsic graphene, we continue to use Mn atom modified porous graphene system, hoping to further improve the adsorption performance of PG system for CH$_4$ molecule.

3.2 Geometric structure of PG system modified by Mn atom

3.2.1 Geometric structure of PG modified by single Mn atom

Firstly, the optimum modification position of single Mn atom on the PG system was studied, and the six initial positions as shown in Fig. 1a were also selected for optimization test. The results show that the Mn atoms at positions 5 and 6 relax to position 1 after optimization, and the Mn atoms at position 2 relax to position 3 after optimization. The Mn atoms at position 4 cannot be adsorbed on the PG system, while the Mn atoms at positions 1 and 3 can be adsorbed stably. The PG system modified by single Mn atom has two stable structures, as shown in Fig. 1b, c. The binding energies of Mn atoms are $-4.017$ eV and $-3.134$ eV, respectively. In Fig. 1b, the binding energy of the Mn atom is the largest and the substrate structure is more stable, which is the optimal modification position of Mn atom in PG system (that is, the central hole of carbon ring). The distance between Mn atom and PG substrate is 1.503 Å.

From Table 1, the Mulliken charge population of the PG before and after Mn-modification (C1–C6 are the six C atoms in the carbon ring where Mn atom is located on the PG substrate). As shown, after Mn atom is adsorbed on PG system, the Mn atom loses 1.11 e, the positive charge increases, the PG substrate gains electrons, the negative charge increases, and the carbon ring surrounded by C1–C6 gets more electrons, forming an evident negative charge center. An electric field is generated between the two, which causes a small part of electrons on C atoms in the PG system to transfer to the lower energy orbital of the Mn atom, resulting in Dewar effect [45]. Figure 3a,c is single Mn decorated PG electron density difference, the blue and yellow isosurface represent the gain and loss of electrons regions, respectively. As shown, most of the surrounding area of the Mn atom is yellow, indicating that the Mn atom has lost electrons, and a small part of the top is blue, indicating that the Mn atom has gained electrons. The C atoms of the base hexagon all gained electrons to form an obvious electronegative center. The larger blue area of the three C atoms (C2, C4, and C6) close to H atoms indicated that more electrons were gained, which was consistent with the Mulliken charge population analysis in Table 1. The loss of electrons from C–C and C–H bonds indicates that the covalent bond is weakened. Ionic bonds are formed between the Mn

![Fig. 2](image-url)  
**Fig. 2** Geometric structure of the optimal adsorption position of single CH$_4$ molecule on the PG system. a is a top view, b is a side view.
atom that loses electrons and the carbon hexagonal ring that gains electrons, and the electron localization function (ELF) gives consistent results. The interaction between Mn and PG can also be seen from the partial state of the density (PDOS) of the Mn-PG system shown in Fig. 4a. In the range of −2.20 to −0.34 eV, the 2p orbital of the C atom and the 3d orbital of the Mn atom overlap strongly. In the range of 0–0.72 eV, the s, p, and d orbitals of the Mn atom overlap with the 2p orbital of the C atom, indicating that there is a strong orbital hybridization between Mn and PG. This action makes the Mn atoms adsorb stably on the PG surface.

### 3.2.2 Geometric structure of PG modified by two Mn atoms

There are three stable structures after the optimization of the PG structure modified by two Mn atoms, as shown in Fig. 5a–c. In Fig. 5a, two Mn atoms are located on the center of two carbon rings on the same side. In Fig. 5b, the two Mn atoms are located on both sides of the same carbon ring center and are symmetrical to the PG surface. In Fig. 5c, two Mn atoms are located on the center of different carbon rings on different sides respectively, showing a centrally symmetric structure relative to the PG substrate. In the structure shown in Fig. 5b, the average binding energy of Mn atom is −3.119 eV, and the substrate is partially deformed and the overall stability of the structure is poor. In Fig. 5a, c, the average binding energy of Mn atom is −4.176 eV and −4.101 eV, respectively. The substrate has no obvious deformation, and the average binding energy value of Mn atom is greater than its cohesion energy −2.920 eV [46], so the possibility of Mn atom aggregation is avoided. When two Mn atoms modify PG system, they can be adsorbed on the same or different sides of different carbon rings.

Figure 3c, d is the electron density difference of two Mn atoms in the center of different carbon rings in the PG. As shown, the Mn atoms lose more electrons when the two Mn atoms modifications PG, and the substrate carbon ring obtains more electrons, so the ionic bonds in the Mn atom and the carbon ring are more obvious. The yellow region of the C–C bond and C–H bond becomes larger, indicating that more electrons are lost and the covalent bond is further weakened. ELF gives consistent results.

| Table 1 | The Mulliken charge population of CH₄ molecule, PG system and Mn-PG system adsorbed for the 1st–6th CH₄ molecules. (charge/e) |
|---------|-------------------------------------------------------------------------------------------------|
|         | H1  | H2  | H3  | H4  | C   | C1  | C2  | C3  | C4  | C5  | C6  | Mn  |
| CH₄     | 0.27| 0.27| 0.28| 0.27| -1.10 | - | - | - | - | - | - | - |
| PG      | - | - | - | - | - | -0.01 | -0.22 | -0.01 | -0.22 | -0.01 | -0.22 | - |
| Mn-PG   | - | - | - | - | - | -0.13 | -0.37 | -0.13 | -0.37 | -0.13 | -0.37 | 1.11 |
| 1st CH₄ | 0.24| 0.28| 0.08| 0.06| -1.05 | -0.13 | -0.37 | -0.15 | -0.37 | -0.13 | -0.37 | 1.56 |
| 2nd CH₄ | 0.27| 0.24| 0.07| 0.11| -1.02 | -0.14 | -0.37 | -0.14 | -0.37 | -0.14 | -0.37 | 1.92 |
| 3rd CH₄ | 0.24| 0.25| 0.22| 0.25| -1.00 | -0.14 | -0.37 | -0.14 | -0.37 | -0.14 | -0.37 | 1.95 |
| 4th CH₄ | 0.25| 0.25| 0.23| 0.20| -0.98 | -0.14 | -0.37 | -0.14 | -0.38 | -0.14 | -0.37 | 1.99 |
| 5th CH₄ | 0.25| 0.27| 0.27| 0.22| -1.03 | -0.14 | -0.37 | -0.15 | -0.37 | -0.15 | -0.36 | 2.00 |
| 6th CH₄ | 0.22| 0.21| 0.22| 0.21| -0.94 | -0.15 | -0.38 | -0.15 | -0.39 | -0.15 | -0.38 | 2.04 |
3.3 Adsorption performance of CH$_4$ on Mn-modified PG system

3.3.1 Adsorption of CH$_4$ on Mn-PG system

The most stable structure of the single Mn atom modified PG system is shown in Fig. 1b. CH$_4$ has several adsorption positions on the Mn-PG system, including Mn atom top, C–C bridge position, hydrocarbon ring hole position, and C atom top position. Studies have discovered that the most stable adsorption site of CH$_4$ molecules is above Mn atom near the C-H bond, as shown in Fig. 6a. At this position, the adsorption energy of the CH$_4$ molecule is $-0.840$ eV, which is much higher than that of CH$_4$ molecule on unmodified
porous graphene (− 0.174 eV). This indicates that Mn atom modification greatly improves the adsorption performance of PG for CH₄ molecules and enhances the adsorption energy of CH₄ molecules on PG. To study the interaction mechanism, Fig. 4b shows the partial density of states of the Mn-PG system when adsorbing a CH₄ molecule. As shown, there is no orbital coupling phenomenon between the 3d orbital of the Mn atom and the orbital of the CH₄ molecule, so there is a weak interaction between the two. The adsorption of the CH₄ molecule on PG belongs to physical adsorption.

To study the adsorption capacity of CH₄ in the Mn-PG system, the adsorption conditions of multiple CH₄ molecules on the Mn-PG system were further calculated. It was discovered that up to 6 CH₄ molecules could be adsorbed on one side, and the optimized structure was shown in Fig. 6 a–f. As shown, CH₄ molecules are mainly adsorbed around Mn atoms or above the carbon ring. When the fifth CH₄ molecule is adsorbed, the adsorption space of CH₄ molecules in the same plane tends to be saturated and stratification occurs. Table 2 lists the continuous adsorption energy (Eₐd), and average adsorption energies (E_avg) of the CH₄ molecule on the PG system. d_Mn-PG represents the distance between the Mn atom and the PG plane, d_Mn-CH₄, d_PG-CH₄ denote the distance between the C atom of the CH₄ molecule and the Mn atom, and the distance between the C atom of the CH₄ molecule and PG plane when Mn-PG system adsorption 1–6 CH₄ molecules. As shown, the distance between the Mn atom and PG plane changes only slightly during the continuous adsorption of CH₄ molecules, which indicates that the two-dimensional structure of the Mn-PG system remains stable and does not deform or collapse with the increase of the number of CH₄ molecules adsorbed.

Table 1 also lists the Mulliken charge population of CH₄ molecule, Mn-PG system, and Mn-PG system adsorb 1–6 CH₄ molecules, in which C and H1-H4 are carbon atoms and four hydrogen atoms on CH₄ molecule, respectively. After the first CH₄ molecule adsorption, Mn atoms lose 0.45 e, and a small number of electrons (0.07 e) transfer to PG substrate further enhance the negative electrical properties.

**Table 2** Energy parameters and geometric parameters of CH₄ molecule adsorption on Mn-PG system. Eₐd(eV) and E_avg(eV) are average adsorption energy and continuous adsorption energy. d_Mn-PG, d_Mn-CH₄, d_PG-CH₄(Å) represent the distance of the Mn atom and the PG plane, the CH₄ molecule and the Mn atom, and the CH₄ molecule and PG plane when Mn-PG system adsorption 1–6th CH₄ molecules, respectively.

| Number of CH₄ | 1     | 2     | 3     | 4     | 5     | 6     |
|--------------|-------|-------|-------|-------|-------|-------|
| Eₐd(eV)      | − 0.840 | − 0.665 | − 0.231 | − 0.133 | − 0.074 | − 0.125 |
| E_avg(eV)    | − 0.840 | − 0.753 | − 0.579 | − 0.467 | − 0.389 | − 0.345 |
| d_Mn-PG(Å)   | 1.528  | 1.558  | 1.554  | 1.557  | 1.550  | 1.605  |
| d_Mn-CH₄(Å)  | 2.169  | 2.327  | 5.357  | 3.881  | 4.354  | 3.678  |
| d_PG-CH₄(Å)  | 3.429  | 3.190  | 3.661  | 3.551  | 5.834  | 3.497  |
of the substrate. The most electrons (0.38 e) transfer to CH₄ molecules, H₃ and H₄ atoms near the Mn atom get electrons 0.20 e and 0.21 e, respectively. H₂ and C atoms lose a small number of electrons, and the molecules show polarity. After the adsorption of the second CH₄ molecule, Mn atom further loses electrons (0.36 e), and H atoms in the CH₄ molecule gain electrons. H₃ and H₄ close to Mn atom get 0.21 e and 0.16 e, respectively. The second CH₄ molecule also shows strong polarity. After adsorption, CH₄ molecules display negatively charged and interact with positively charged the Mn atom, which enhances the adsorption performance of CH₄ molecules. As the number of CH₄ molecules increases, the adsorption energy of CH₄ molecules decreases. When the third to sixth CH₄ molecules are adsorbed, the distance between CH₄ molecules and Mn atoms is longer, the charge transfer is less, and the electrostatic interaction is weakened. However, the modification of the Mn atom enhances the overall electronegativity of PG substrate and forms the negative charge center. It makes the surface of CH₄ molecule with positive electricity on the PG surface far away from the modified atom; the adsorption can also be produced, which is mainly caused by the interaction between the positive charge on the surface of CH₄ and the PG substrate with the negative charge. The adsorption energy of the fifth CH₄ molecule is much lower than that of the other CH₄ molecules because the stratification phenomenon occurs during the adsorption of the fifth CH₄ molecule, which makes the CH₄ molecule far from the PG substrate, so the interaction is weakened. The sixth CH₄ molecule is closer to the PG surface than the fifth CH₄ molecule, which is located on the first layer of CH₄ molecule adsorption. The addition of the sixth CH₄ molecule makes the position of most of the original CH₄ molecules relax, so the adsorption energy is increased compared with the fifth CH₄ molecule. The Mn-PG system adsorbed six CH₄ molecules on one side, one more CH₄ molecule than the Mn-modified intrinsic graphene system [39], and the number of porous graphene atoms was less than that of intrinsic graphene, so the adsorption capacity of the CH₄ molecule was improved.

Figure 7 shows the electron density difference of Mn-PG system adsorbing 1–3 CH₄ molecules. The blue and yellow isosurface represent the electron gain and electron loss regions, respectively. As shown, there are more electron transfer between the first and second CH₄ molecules and Mn atoms, CH₄ molecules show obvious polarity after adsorption, and CH₄ molecules have strong interaction, so the adsorption energy is larger, and the number of CH₄ molecules is promoted. The electron transfer of the third to sixth CH₄ molecules is less, which is not obvious in the same precision electron density difference, which is the same as the result of Mulliken charge population analysis. The polarity and intermolecular interaction of CH₄ molecules are weakened after adsorption. They are mainly due to the electrostatic interaction between the positive charge on the surface of CH₄ molecule and the negatively charged PG substrate.

3.3.2 Adsorption of CH₄ on 2Mn-PG system

When the PG system is modified by two Mn atoms, the energies of the two stable structures shown in Fig. 5a, c are nearly the same. After the adsorption test of CH₄ molecule, it is discovered that the substrate in Fig. 5a will undergo obvious bending deformation after the CH₄ molecule is adsorbed. This is because the two Mn atoms on the same
side of the PG plane have an electrostatic interaction with the CH$_4$ molecule and the strong force between the Mn atom itself and carbon ring, so that the PG substrate is bent to the CH$_4$ molecule, destroying its two-dimensional structure. The structure in Fig. 5c remains a stable two-dimensional structure after the adsorption of CH$_4$. Therefore, the structure in Fig. 5c is selected to study the adsorption performance of CH$_4$ molecules in the 2Mn-PG system.

In the 2Mn-PG system, 12 CH$_4$ molecules can be adsorbed on both sides, and 6 CH$_4$ molecules can be adsorbed on each side. The optimized geometric structures are shown in Fig. 8a-l. As shown, the distance between the two Mn atoms and PG remains unchanged during the continuous adsorption of CH$_4$, and the two-dimensional structure of the substrate is stable. The adsorption position of CH$_4$ molecule is the same as that of single Mn atom. Each side of CH$_4$ molecule is first adsorbed near Mn atom, and the Mn atom plays an important role in the adsorption process of CH$_4$ molecule. The first to fourth CH$_4$ molecules are adsorbed on one side in the same plane. When the fifth CH$_4$ molecule is adsorbed, because the repulsive force between CH$_4$ molecules, a large number of CH$_4$

![Fig. 8](image_url)
molecules cannot coexist in the same plane, so stratification occurs. At the same time, CH$_4$ molecules in the first layer relax, and the adsorption space reaches saturation after the adsorption of six CH$_4$ molecules. When CH$_4$ molecules adsorbed on both sides of the system are saturated, the overall structure is more symmetrical. Figure 9 shows the continuous adsorption energy $E_{ad}$, the average adsorption energy $\overline{E}_{ad}$ of CH$_4$ molecules in the 2Mn-PG system, and the distance $d_{PG-CH_4}$ from the CH$_4$ molecule to the PG plane. As shown, the distance between the CH$_4$ molecules in the first layer on each side and the PG surface is 3–4 Å, and the adsorption energy decreases with the increase in the number of CH$_4$ molecules adsorption, ranging from $-0.853$ eV to $-0.114$ eV. The distance between the CH$_4$ molecules in the second layer and the PG surface is more than 5 Å, and the adsorption energy is generally lower than $-0.100$ eV. This is because the distance between the CH$_4$ molecules in the second layer and the PG surface is far, and the interaction between the positively charged CH$_4$ molecules on the surface and the negatively charged PG substrate is weakened and the adsorption energy is low. When 12 CH$_4$ molecules were adsorbed, the average adsorption energy was $-0.338$ eV, and the adsorption capacity was up to 38.43 wt.%. It is close to the CH$_4$ average adsorption energy of the 2Mn-GR system ($-0.402$ eV) and Ag modified graphene in the presence of ambient O$_2$ ($-0.399$ eV) [28, 39]. And the CH$_4$ average adsorption energy is higher than two Ti atoms modified graphyne and two Ti atoms modified C$_6$H$_2$ type PG (2Ti-PG-C$_6$H$_2$) substrates ($-0.300$ eV, $-0.207$ eV) [47, 48]. Although the adsorption capacity is reduced compared to the 2Ti-PG-C$_6$H$_2$ system (54.7 wt.%), the average adsorption energy of 2Mn-PG system is higher. Compared with the 2Mn-GR system (32.93 wt.%), the adsorption capacity of 2Mn-PG system is increased by 5.5 wt.%, which is closer to the energy storage target proposed by the U.S. DOE. Therefore, 2Mn-PG is a more promising CH$_4$ storage material that balances adsorption energy and adsorption capacity.

To further verify the structural stability and eliminate the influence of edge effect, a $2 \times 2$ supercell was established based on the above PG structure, which contains 96 C atoms, 216 H atoms, and eight modified Mn atoms. This structure can adsorb 48 CH$_4$ molecules, and the optimized geometry is shown in Fig. 10. The results show that the average binding energy of the Mn atom is $-4.045$ eV, which is larger than the cohesive energy and avoids the agglomeration. The average adsorption energy of CH$_4$ molecule is $-0.292$ eV, which is less different from the calculation results of the primitive cell. It shows that the system structure is stable, and the calculation results are reasonable. There is no CH$_4$ molecule adsorption at the center of the supercell, which is due to the large pore size of the PG structure. The CH$_4$ molecule located here is far away from the negative charge center of the substrate and Mn atoms, and the interaction force is too weak for adsorption to occur. Therefore, the pore size has a great influence on the adsorption performance of CH$_4$ molecules. We will conduct subsequent studies on the adsorption performance of CH$_4$ by adjusting the pore size of the PG system.
4 Conclusion

Based on first-principles density functional theory, the adsorption properties of PG and Mn-PG systems for CH₄ molecules were studied, and the following conclusions were obtained:

(1) The optimum adsorption location of CH₄ molecule on porous graphene is the carbon rings hole position, with the adsorption energy of −0.174 eV and the distance between CH₄ molecule and PG substrate is 3.353 Å.

(2) The optimal position of the PG system modified by single Mn atom is the hexagonal carbon ring hole position. When two Mn atoms modified the PG system, only the system with two Mn atoms located at different carbon rings hole sites on the opposite side can maintain structural stability when CH₄ was adsorbed, and the average binding energy is −4.101 eV. The charge transfer between Mn atoms and PG substrate resulted in strong orbital hybridization, and the ionic bond is formed from the carbon hexagonal ring, which made it stably modified on PG surface. The modification of Mn atom enhances the electronegativity of PG substrate and generates a negative charge center at the carbon ring, which is beneficial to enhance the adsorption performance of CH₄ molecules with positive charge on the surface.

(3) Mn atom modification can improve the adsorption performance of CH₄ molecules in the PG system. The best adsorption position of single CH₄ molecule in the Mn-PG system is above Mn atom near the C-H bond, and the adsorption energy can reach −0.840 eV, which belongs to physical adsorption. The CH₄ molecule close to the Mn atom shows negatively charged and has a strong electrostatic interaction with the positively charged Mn atom, which plays a major role in the adsorption. The adsorption energy is large, and the molecules have polarity, which reduces the intermolecular repulsion and is conducive to the increase in the adsorption number of CH₄ molecules. The surface of CH₄ molecule far away from Mn atom is positively charged, and the weak electrostatic interaction with negatively charged PG substrate is dominant in the adsorption, and the adsorption energy is low. The CH₄ molecules are adsorbed on the PG surface through the electrostatic interaction with Mn atoms and PG substrates as well as the synergistic effect of the intermolecular forces of CH₄.

(4) The Mn-PG system can adsorb 6 CH₄ molecules on one side, and the average adsorption energy is −0.345 eV. 2Mn-PG can adsorb 12 CH₄ molecules on both sides with an average adsorption energy of −0.338 eV and an adsorption capacity of 38.43 wt.%, which is close to the energy storage target proposed by the U.S. DOE. Therefore, PG is a kind of CH₄ storage material with good development prospects.

Acknowledgements The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (Grant Number 51502022), the Basic Scientific Research Foundation for Gansu Universities of China (Grant Number 05-0342), and the Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (second phase).

Author contribution QZ contributed to the theoretical calculation and thesis writing and paper revision; YZ contributed to the theoretical calculation and thesis writing; YC contributed to provide ideas and paper revision; JJ contributed to auxiliary data calculation; WX contributed to auxiliary data calculation; MZ contributed to data research method; CS contributed to data research method; CZ contributed to provide ideas and methods (The two authors QZ and YZ contributed equally to this work and should be considered co-first authors.)

Data availability All research results and data have been included in the manuscript, and the data of this research results can be obtained from the corresponding author according to reasonable requirements.

References

1. M.Z. Jacobson, Control of fossil-fuel particulate black carbon and organic matter, possibly the most effective method of slowing global warming. J. Geophys. Res. Atmos. 107, 16–22 (2002)
2. F. Keppeler, J.T. Hamilton, M. Brass, T. Rockmann, Methane emissions from terrestrial plants under aerobic conditions. Nature 439, 187–191 (2006)
3. T.A. Makal, J.R. Li, W. Lu, H.C. Zhou, Methane storage in advanced porous materials. Chem. Soc. Rev. 41, 7761–7779 (2012)
4. D.R. Feldman, W.D. Collins, S.C. Biraud, M.D. Risser, D.D. Turner, P.J. Gero, J. Tadić, D. Helmg, S. Xie, E.J. Mlawer, T.R. Shippert, M.S. Torn, Observationally derived rise in methane surface forcing mediated by water vapour trends. Nat. Geosci. 11, 238–243 (2018)
5. D. Fraenkel, J. Shabtai, Encapsulation of hydrogen in molecular sieve zeolites. J. Am. Chem. Soc. 99, 7074–7076 (1977)
6. S.J. Chen, W. Dai, J.S. Luo, Y.J. Tang, C.Y. Wang, W.G. Sun, Simulation of methane adsorption in AFS molecular sieves. Acta Phys. Chim. Sin. 25, 285–290 (2009)
7. A. Policicchio, E. Maccallini, R.G. Agostino, F. Ciuchi, A. Aloise, G. Giordano, Higher methane storage at low pressure and room temperature in new easily scalable large-scale production activated carbon for static and vehicular applications. Fuel 104, 813–821 (2013)
8. H. Furukawa, O.M. Yaghi, Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy applications. J. Am. Chem. Soc. 131, 8875–8883 (2009)
9. H. Wu, J.M. Simmons, Y. Liu, C.M. Brown, X.-S. Wang, S. Ma, V.K. Peterson, P.D. Southon, C.J. Kepert, H.-C. Zhou, T. Yildirim, W. Zhou, Metal-organic frameworks with exceptionally high...
methane uptake: Where and how is methane stored? Chem.-A Eur. J. 16, 5205–5214 (2010)

10. S. Ma, H.-C. Zhou, Gas storage in porous metal-organic frameworks for clean energy applications. Chem. Commun. 46, 44–53 (2010)

11. V.C. Menon, S. Komarneni, Porous adsorbents for vehicular natural gas storage: a review. J. Porous Mater. 5, 43–58 (1998)

12. J. Liu, R. Zou, Y. Zhao, Recent developments in porous materials for H₂ and CH₄ storage. Tetrahedron Lett. 57, 4873–4881 (2016)

13. V. Rozzeyev, D. Thirion, R. Ullah, J. Lee, M. Jung, H. Oh, M. Atilhan, C.T. Yavuz, High-capacity methane storage in flexible alkane-linked porous aromatic network polymers. Nat. Energy 4, 604–611 (2019)

14. J.M. Lin, C.T. He, Y. Liu, P.Q. Liao, D.D. Zhou, J.P. Zhang, X.M. Chen, A metal-organic framework with a pore size/shape suitable for strong binding and close packing of methane. Angew Chem. Int. Ed. Engl. 55, 4674–4678 (2016)

15. Z. Chen, P. Li, R. Anderson, X. Wang, X. Zhang, L. Robison, L.R. Redfern, S. Moribe, T. Islamoglu, D.A. Gomez-Gualdrón, T. Yildirim, J.F. Stoddart, O.K. Farha, Balancing volumetric and gravimetric uptake in highly porous materials for clean energy. Science 368, 297–303 (2020)

16. Y. Yan, D.I. Kolokolov, I. da Silva, A.G. Stepanov, A.J. Blake, A. Dailly, P. Manuel, C.C. Tang, S. Yang, M. Schroder, Porous metal-organic polyhedral frameworks with optimal molecular dynamics and pore geometry for methane storage. J. Am. Chem. Soc. 139, 13349–13360 (2017)

17. C.C. Liang, Z.L. Shi, C.T. He, J. Tan, H.D. Zhou, H.L. Zhou, Y. Lee, Y.B. Zhang, Engineering of pore geometry for ultrahigh capacity methane storage in mesoporous metal-organic frameworks. J. Am. Chem. Soc. 139, 13300–13303 (2017)

18. J. Jiang, H. Furukawa, Y.B. Zhang, O.M. Yaghi, High methane storage working capacity in metal-organic frameworks with acrylic links. J. Am. Chem. Soc. 138, 10244–10251 (2016)

19. A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C.N. Lau, Superior thermal conductivity of single-layer graphene. Nano Lett. 8, 902–907 (2008)

20. C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science 321, 385–388 (2008)

21. R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber, N.M.R. Peres, A.K. Geim, Fine structure constant defines visual transparency of graphene. Science 320, 1308–1308 (2008)

22. H.B. Heersche, P. Jarillo-Herrero, J.B. Oostinga, L.M.K. Vandersypen, A.F. Morpurgo, Bipolar supercurrent in graphene. Nature 464, 56–59 (2007)

23. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Electric field effect in atomically thin carbon films. Science 306, 666–669 (2004)

24. D. Yang, N. Yang, J. Ni, J. Xiao, J. Jiang, Q. Liang, T. Ren, X. Chen, First-principles approach to design and evaluation of graphene as methane sensors. Mater. Des. 119, 397–405 (2017)

25. M.D. Ganji, H. Mazingher, A. Khorasani, Acetone adsorption on pristine and pt-doped graphene: a first-principles vD-WDF Study. Commun. Theor. Phys. 64, 576–582 (2015)

26. M. Gautam, A.H. Jayatissa, Ammonia gas sensing behavior of graphene surface decorated with gold nanoparticles. Solid-State Electron. 78, 159–165 (2012)

27. M. Zhou, Y.H. Lu, Y.Q. Cai, C. Zhang, Y.P. Feng, Adsorption of gas molecules on transition metal embedded graphene: a search for high-performance graphene-based catalysts and gas sensors. Nano-technology 22, 385502–385509 (2011)

28. R. Ghanbari, R. Safaee, M.M. Golshan, A dispersion-corrected DFT investigation of CH₄ adsorption by silver-decorated monolayer graphene in the presence of ambient oxygen molecules. Appl. Surf. Sci. 457, 303–314 (2018)

29. A.S. Rad, H. Pazoki, S. Mohseni, D. Zareyee, M. Peyravi, Surface study of platinum decorated graphene towards adsorption of NH₃ and CH₄. Mater. Chem. Phys. 182, 32–38 (2016)

30. L. Jiang, Z. Fan, Design of advanced porous graphene materials: from graphene nanomesh to 3D architectures. Nanoscale 6, 1922–1945 (2014)

31. A. Du, Z. Zhu, S.C. Smith, Multifunctional porous graphene for nanoelectronics and hydrogen storage: new properties revealed by first principle calculations. J. Am. Chem. Soc. 132, 2876–2877 (2010)

32. L.D. Carr, M.T. Lusk, Defect engineering: graphene gets designer defects. Nat Nanotechnol. 5, 316–317 (2010)

33. Z. Ao, S. Dou, Z. Xu, Q. Jiang, G. Wang, Hydrogen storage in porous graphene with Al decoration. Int. J. Hydrogen Energy 39, 16244–16251 (2014)

34. M. Bieri, M. Treier, J. Cai, K. Ait-Mansour, P. Ruffieux, O. Groning, P. Groning, M. Kastler, R. Rieger, X. Feng, K. Muller, R. Fasel, Porous graphene: two-dimensional polymer synthesis with atomic precision. Chem. Commun. (Camb) 45, 6919–6921 (2009)

35. Y. Chen, J. Wang, L. Yuan, M. Zhang, C. Zhang, Sc-Decorated porous graphene for high-capacity hydrogen storage: first-principles calculations. Materials (Basel) 10, 894–904 (2017)

36. L. Yuan, Y. Chen, L. Kang, C. Zhang, D. Wang, C. Wang, M. Zhang, X. Wu, First-principles investigation of hydrogen storage capacity of Y-decorated porous graphene. Appl. Surf. Sci. 399, 463–468 (2017)

37. J.O. Abe, A.P.I. Popoola, E. Ajenifuje, O.M. Popoola, Hydrogen energy, economy and storage: review and recommendation. Int. J. Hydrogen Energy 44, 15072–15086 (2019)

38. https://www.energy.gov/oe/fuelscells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles.

39. Y. Zhao, Y. Chen, M. Song, X. Liu, W. Xu, M. Zhang, C. Zhang, Methane adsorption properties of mn-modified graphene: a first-principles study. Adv. Theory Simul. 3, 2000035–2000043 (2020)

40. W. Xu, Y. Chen, Y. Zhao, M. Zhang, R. Tian, C. Zhang, Methane adsorption properties of N-doped graphene: a first-principles study. Struct. Chem. 32, 1517–1527 (2021)

41. M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, First-principles simulation: ideas, illustrations and the CASTEP code. J. Phys.: Condens Matter 14, 2717–2744 (2002)

42. J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996)

43. T. Bjorkman, A. Gulans, A.V. Krasheninnikov, R.M. Nieminen, van der waals bonding in layered compounds from advanced density-functional first-principles calculations. Phys. Rev. Let. 108, 235502–235506 (2012)

44. D. Rao, R. Lu, Z. Meng, Y. Wang, Z. Lu, Y. Liu, X. Chen, E. Kan, C. Xiao, K. Deng, H. Wu, Electronic properties and hydrogen storage application of designed porous nanotubes from a polyphenylene network. Int. J. Hydrogen Energy 39, 18066–18975 (2014)

45. D. Michael, P. Mingos, A historical perspective on Dewar’s landmark contribution to organometallic chemistry. J. Organomet. Chem. 635, 1–8 (2001)

46. C. Kittel, H.Y. Fan, Introduction to solid state physics. Am. J. Phys. 25, 330–330 (1957)

47. W. Xu, Y. Chen, Y. Zhao, M. Zhang, R. Tian, C. Zhang, First-principles study on the methane adsorption properties by Ti-modified graphene. Int. J. Quantum Chem. 23, e26811 (2021)

48. Y.J. Zhao, Y.H. Chen, W.H. Xu, M.L. Zhang, C.R. Zhang, First-principles study on methane adsorption performance of ti-modified porous graphene. Phys. Status Solidi (b) (2021). https://doi.org/10.1002/pssb.202100168

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.