

## Electric Field Controlled Separation and Capture of CO<sub>2</sub> over S-Doped Graphene: A First-Principles Calculation

<sup>1</sup>Jingyi Shan, <sup>1</sup>Xiangling Wang, Junkai Wang\*, Shixuan Zhang, Qianku Hu and Aiguo Zhou  
*School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454003, China.*  
jkwang@hpu.edu.cn\*

(Received on 19<sup>th</sup> November 2020, accepted in revised form 1<sup>st</sup> June 2021)

**Summary:** The selective adsorption and capture of CO<sub>2</sub> from post-combustion gases carries huge significance for the reduction of greenhouse effect. In this research, the computations of density functional are performed to investigate the CO<sub>2</sub> selective adsorption of S-doped graphene in thrall to applied electric field (E-F). Introducing the applied E-F, the adsorption between S-doped graphene and CO<sub>2</sub> is strong chemisorption, and CO<sub>2</sub> can be effectively captured. Removing the applied E-F, the adsorption restores to physisorption and CO<sub>2</sub> is easily desorbed. Therefore, the CO<sub>2</sub> seize and clearing can be realized merely by controlling the E-F. Besides, the adsorption energy of N<sub>2</sub> (H<sub>2</sub>O) on S-decorated graphene is positive when introduce the applied E-F. The results demonstrated that S-doped graphene can selectively adsorb CO<sub>2</sub> from the post-combustion gases by controlling the E-F.

**Key words:** CO<sub>2</sub> separation and capture; S-doped graphene; Greenhouse effect; First-principles calculation.

### Introduction

In recent decades, greenhouse gases have been the focus of attention because they are the main cause of environmental change. Among these greenhouse gases, CO<sub>2</sub> is the one possesses high value of global warming potential. As people's growing demand for energy, the human activities such as deforestation, car industry process powered by natural gas and the burning of fossil fuels, have caused the crazy increase of CO<sub>2</sub> concentration in air. This has seriously affected the human health and earth's environment such as global warming [1-3]. Thus, efficient separation of CO<sub>2</sub> from the post-combustion gases (mainly CO<sub>2</sub>/N<sub>2</sub> mixture) is an urgent task at present [4].

As a novel two-dimensional nanomaterial with atom-thick sp<sup>2</sup> hybridized carbon atoms, graphene have attracted extensive attentions because of its greater specific superficial area, leading thermal, high Young's modulus and tremendous mechanical strength and excellent chemical properties [5-7]. However, pristine graphene does not show a great ability to capture CO<sub>2</sub> because the interaction between pure graphene and CO<sub>2</sub> molecules belongs to the category of physical adsorption and it has weak adsorb ability for CO<sub>2</sub> molecules [8]. Therefore, numerous works paid their attention on tailoring the surface activity and adsorb ability of pure graphene via element doping [9-11]. In this way, strong chemisorptions between doped graphene and CO<sub>2</sub> could be obtained with the proper doping elements [12-13]. For example, in the calculation performed by Cortés-Arriagada *et al.*, the E<sub>ads</sub> of CO<sub>2</sub> adsorbed onto

pristine graphene is only -0.11 eV, and this value increases to -0.54 eV when the CO<sub>2</sub> onto Fe-doped grapheme [11]. Similar results are also obtained by Oh *et al.* [14].

Electric field (E-F) is a clean resource, which can be easily manipulated and adjusted. In recent years, the results of numerous works suggest that the interaction between CO<sub>2</sub> molecular and adsorbent could be tailored by applying an E-F [15-18]. For example, the study by Guo and coworkers reveal that two-dimensional BN monolayer can capture CO<sub>2</sub> selectively among H<sub>2</sub>O, N<sub>2</sub>, CH<sub>4</sub>, CO, and H<sub>2</sub> gaseous mixture by applying an E-F of 0.030 a.u. [16]. Moreover, Sun *et al.* [17] reveals that the CO<sub>2</sub> is physically adsorbed on the MoS<sub>2</sub> nanosheet without an E-F, and the physical adsorption converts to chemical adsorption when the E-F enlarge to 0.004 a.u.. More recently, the interaction between P-doped graphene and CO<sub>2</sub> has also been investigated [18]. The results show that CO<sub>2</sub> weakly adsorbed on P-doped graphene without any E-F. However, CO<sub>2</sub> is strongly chemisorbed onto P-doped graphene by applying an E-F of 0.013-0.020 a.u. What's more, by shutting down the E-F, the captured CO<sub>2</sub> molecules release from the P-doped graphene easily.

Compared with P-decorated graphene, S-decorated graphene is expected to display more active surface and chemical properties since the doping atom S has more valence electrons than P atom. At present, S-doped graphene have been successfully prepared experimentally [19-24]. However, CO<sub>2</sub> adsorption and

\*To whom all correspondence should be addressed.

<sup>1</sup>These two author contributed equally to this work

separation performances on S-doped graphene nanosheet in an external E-F have yet to be elucidated distinctly.

In our current research, CO<sub>2</sub> adsorption on S-doped graphene under an external E-F was investigated and the probability of employing S-doped graphene as the material for CO<sub>2</sub> efficient collection was studied. Moreover, to further clarify the adsorption/release mechanism of CO<sub>2</sub>, the electronic structure analysis of CO<sub>2</sub> and S-doped graphene were also carried out. From what we know so far, it is the first theoretical studies on these issues. The results of our study could present a meaningful method for the abruption of CO<sub>2</sub> from post-combustion gases (CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O) on S-doped graphene under the assistance of adsorptive E-F.

### Computational Methods

In this paper, Dmol<sup>3</sup> package [25] in Materials Studio Software (MSS) is used for first principle calculation. All calculations were performed using generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) functional [26-27]. In the calculation process, the DFT semi-core pseudopotential [28] and Grimme method [29-30] were chose, and a double numeric basis set augmented by polarization function (DNP) is selected. In this work, the BSSE correction is not taken into consideration [31-33].

The 6 × 6 unit cell is adopted. When geometric optimization, all atoms in the model are completely relaxed and unconstrained. In addition, the constriction criteria of energy, maximum shifting and force parameters are 10<sup>-5</sup> Hartree, 0.005 Å and 0.002 Hartree/Å, respectively. A 30 Å empty space is used in the z orientation. The k-point lattice in Brillouin area is divided by Monkhorst-Pack [34]. For geometry optimizations and density of states, 3 × 3 × 1 and 15 × 15 × 1 k-points mesh are adopted, respectively.

The E<sub>ads</sub> between gas molecule and the pure/S-doped graphene nanosheets are defined as:

$$E_{\text{ads}} = E_{\text{gas/graphene}} - (E_{\text{graphene}} + E_{\text{gas}}) \quad (1)$$

$$E_{\text{ads}} = E_{\text{gas/S-doped graphene}} - (E_{\text{S-doped graphene}} + E_{\text{gas}}) \quad (2)$$

where E<sub>gas/graphene</sub>, E<sub>graphene</sub>, E<sub>gas</sub>, E<sub>gas/S-doped graphene</sub> and E<sub>S-doped graphene</sub> deputy the overall energy of original

graphene, graphene sheet, gas molecule, gas adsorption the S-doped graphene and S-decorated graphene, respectively. Hirshfeld charge distribution [35] is used to analyze the charge transfer.

### Results and Discussion

#### Structure evolution and properties of S-doped graphene

The structures of pristine graphene and S doped graphene after optimization are presented in Fig. 1. In the pristine graphene (Fig. 1a), the C-C bond length was 1.424 Å, which is equal to reported literatures [36-37]. When decorated with the S atom (Fig. 1b), the S-C bond lengths connected to the S atom were increased to 1.763 Å and S atom was jacked up by 1.266 Å, which can be attributed to the radius difference of C and S atom. Based on charge analysis, all of the C atoms were zero charge state in original graphene. However, after replacing one C with S atom, the substitutional S atom obtains -0.109 e electrons from its neighboring C atoms, suggesting that S can be recognized as an active center of CO<sub>2</sub> adsorption.

To further understand the changes of electronic structure after S doping, the density of state of S doped and pristine graphene was calculated and presented in Fig. 2. Upon doping with S atom, it was discovered that the electronic density of states (close to Fermi energy) perceptibly mounted and the electrical conductivity elevated. According to reported literatures, the charge transfer of the basis to the adsorbed gases mainly affected by these characteristics [38, 39]. Consequently, the doping of S atom can cause the variation of electron density from the nearby Fermi energy, which leads to the enhancement of chemical sensitivity of S-doped graphene system.

#### Adsorption of CO<sub>2</sub> on S-doped graphene without an E-F

To clarify the adsorption behavior and mechanism of CO<sub>2</sub> on S-decorated graphene without the E-F, two kinds of initial configurations of CO<sub>2</sub> are considered (Fig. 3). The first one is CO<sub>2</sub> parallel to the S-decorated graphene with three atoms of CO<sub>2</sub> draw near the nanosheet (Fig. 3a). The second one is three atoms of CO<sub>2</sub> and S atom are in a vertical line and only one of the O atom towards the nanosheet (Fig. 3b).

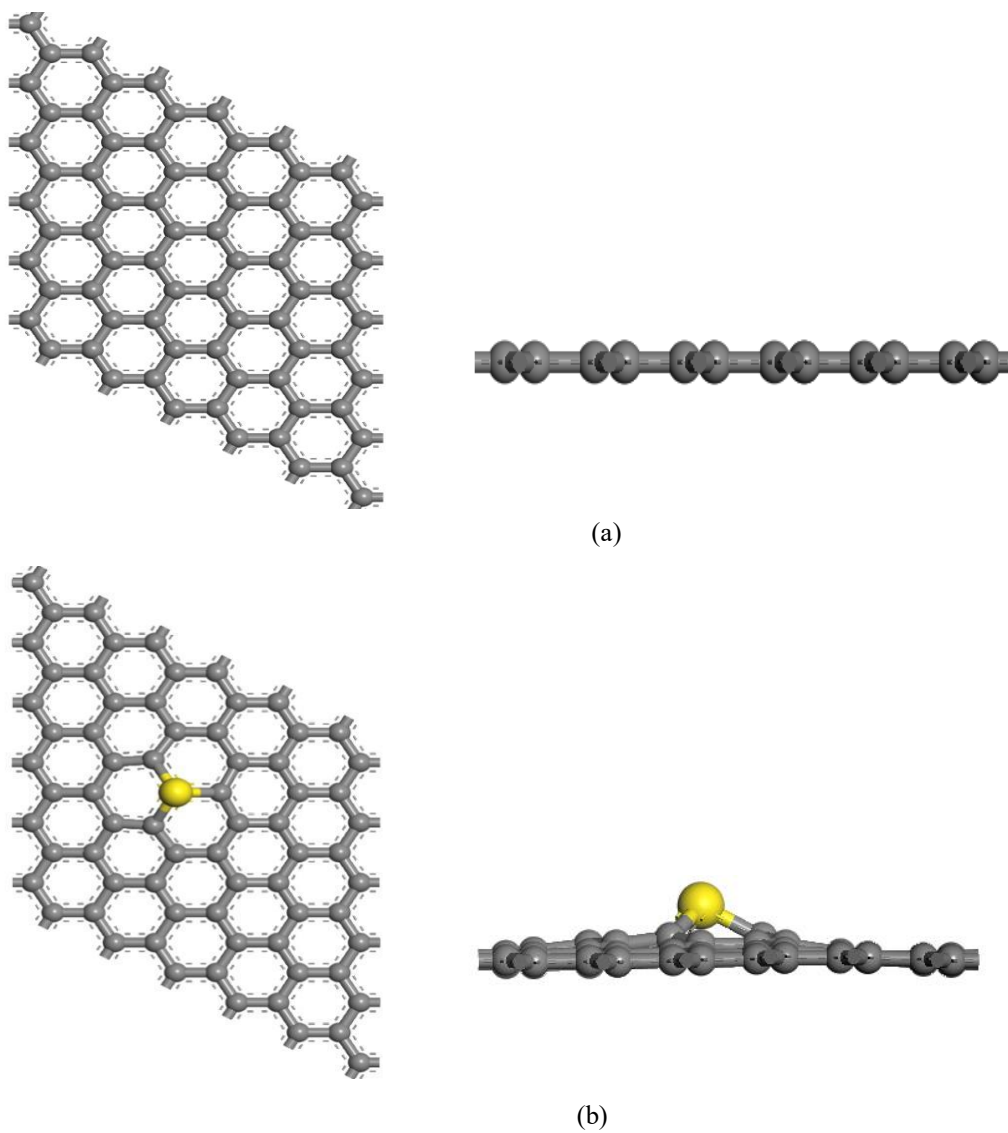


Fig. 1: View from the top and the side of pristine graphene (a) and S-doped graphene.

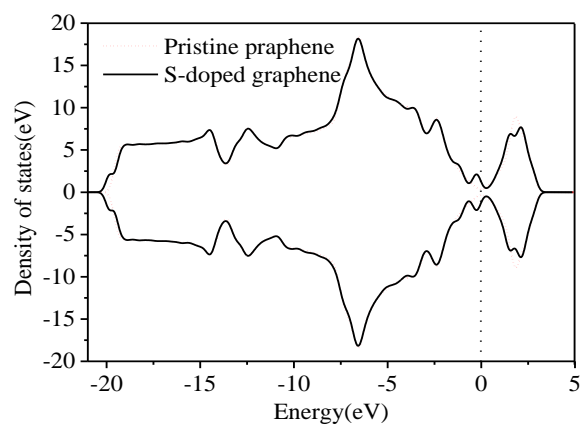


Fig. 2: The DOS of the pristine graphene and S-doped graphene. The dotted black line represents the Fermi level, set to zero.

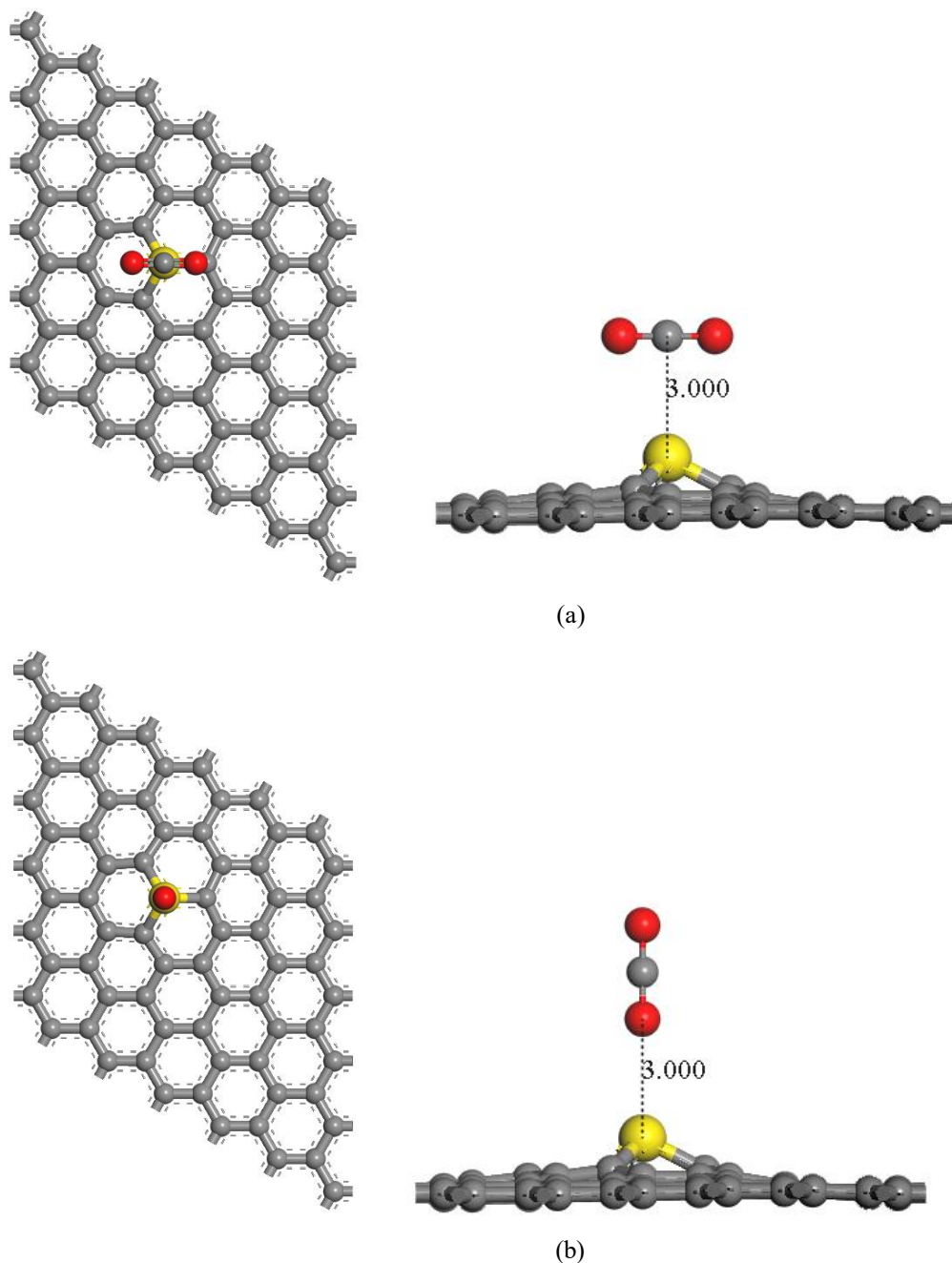


Fig. 3: The initial configurations of CO<sub>2</sub> on S-doped graphene sheet.(a) CO<sub>2</sub> was parallel to the S-doped graphene sheet; (b) CO<sub>2</sub> was perpendicular to the S-doped graphene sheet with the oxygen atom close to the sheet.

After geometry relaxation (Fig. 4), the  $E_{\text{ads}}$  of the first configuration is bigger than the second, indicating that CO<sub>2</sub> molecular is more probably parallel with S-doped graphene via the interaction between C and S atom. This suggests that the interplay

between C atom and S atom are greater than that O and S atoms. However, it is to be noted that the  $E_{\text{ads}}$  between CO<sub>2</sub> and S-decorated graphene in the first case is only -0.07eV, indicating the weak interaction and physisorption nature of the adsorption system.

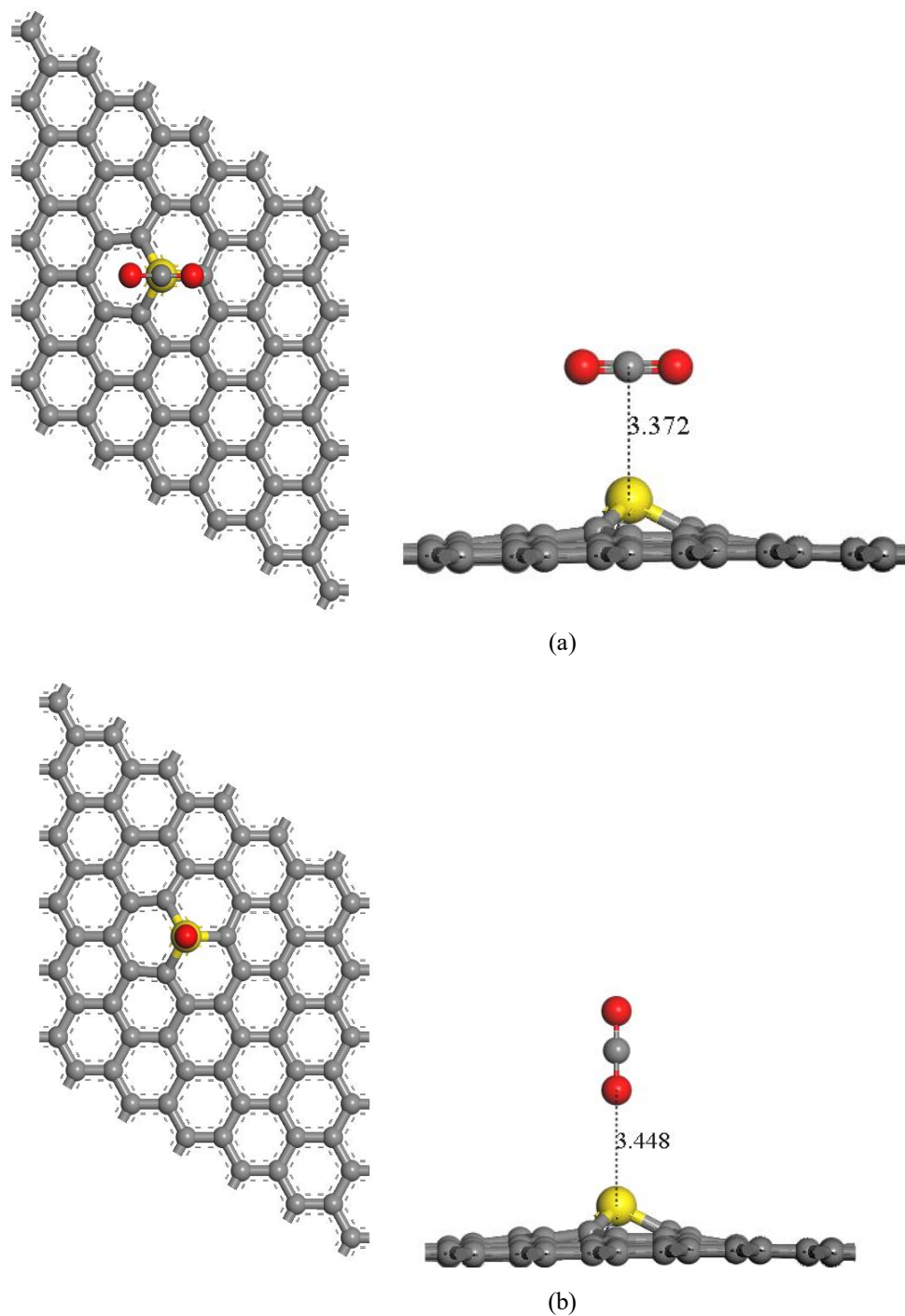


Fig. 4: The optimized structure of CO<sub>2</sub> adsorbed S-doped graphene sheet. Bond distances are in Å.

According to Hirshfeld charge density analysis, only  $-0.016|e|$  electron shift from S-doped graphene to CO<sub>2</sub> is observed. As a consequence, compared to the free standing CO<sub>2</sub> molecule, there is no significant structure change for the adsorbent CO<sub>2</sub>

molecule. All the above observations indicate that CO<sub>2</sub> is physisorbed on S-doped graphene without an E-F, and this S-doped graphene cannot be adopted directly as an effective adsorbent to collect CO<sub>2</sub> in normal environment.

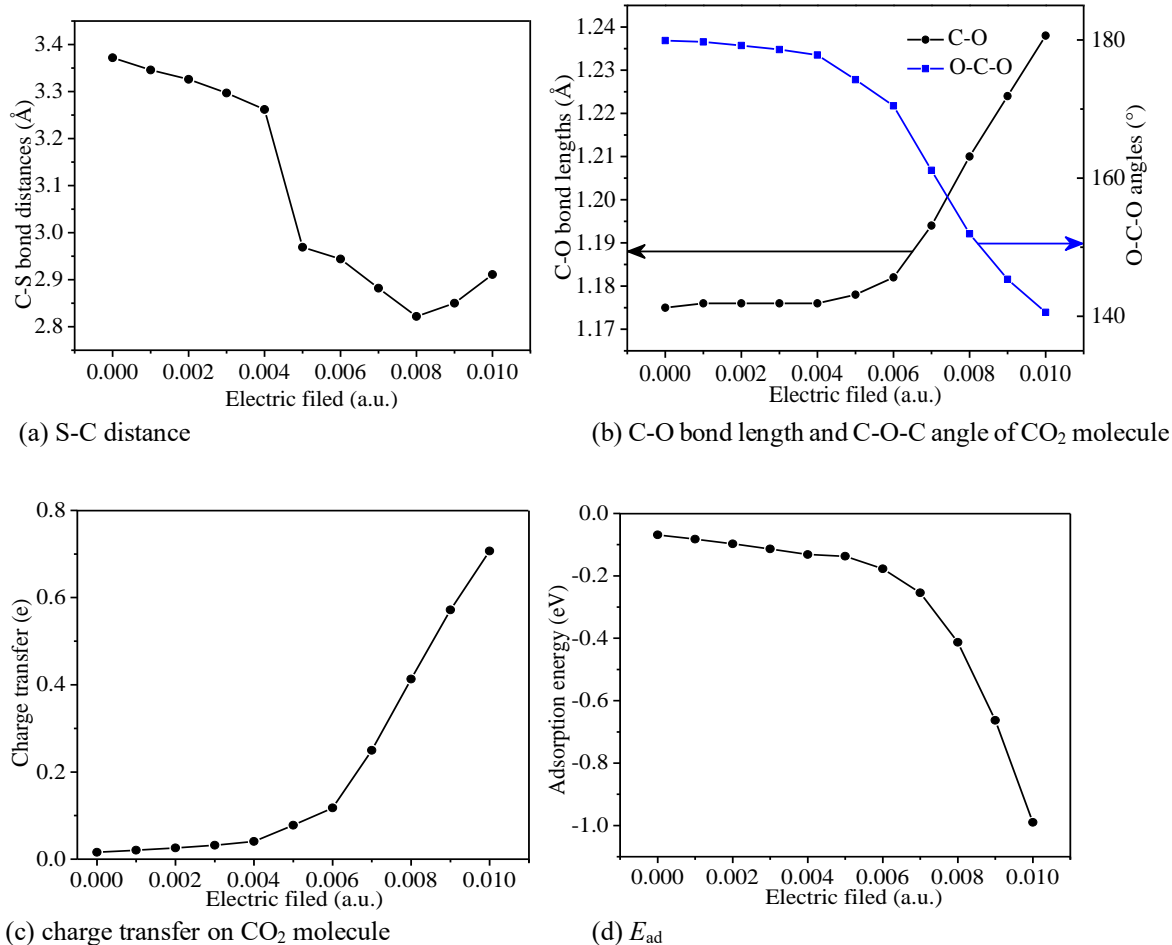


Fig. 5: Variation of (a) S-C distance, (b) C-O bond length and C-O-C angle of CO<sub>2</sub> molecule, (c) charge transfer on CO<sub>2</sub> molecule and (d) E<sub>ad</sub> under various E-F.

#### Adsorption of CO<sub>2</sub> on S-doped graphene with the E-F

To regulate the adsorption properties of S-decorated graphene sheet, the CO<sub>2</sub>/S-decorated graphene is subject to a perpendicular E-F with the range of 0–0.010 a.u. (along the z orientation). Fig. 5 presents the change trend of binding distances, C-O bond lengths and C-O-C angles, electron-transfer and E<sub>ads</sub> of CO<sub>2</sub> as the increasing of the E-F intensity. The corresponding optimized configurations under E-F = 0.001, 0.006, 0.007 and 0.009 a.u. are also presented in Fig. 6. In Fig. 5a, we can see clearly that as E-F changed from 0.001 to 0.006 a.u., the binding distances of S-doped graphene and CO<sub>2</sub> decreased slightly. Particularly, the binding distance at E-F = 0.006 a.u. is 2.944 Å, which is approximately 0.402 Å shorter than at E-F = 0.001 a.u. Moreover, the C-O bond length increases 0.006 Å, and the O-C-O angle only decreases 9.2°, showing that CO<sub>2</sub> warps

slightly on S-doped graphene (Fig. 6a and b). These results are also in consonance with the negligible charge transfer increase from S-doped graphene to CO<sub>2</sub> (Fig. 5c). The presented E<sub>ads</sub> further verify the above inference, where the E<sub>ads</sub> of CO<sub>2</sub> mounted into approximately 0.11 eV when the E-F value reached to 0.006 a.u.. These results vividly prove that the interaction of CO<sub>2</sub> and S-doped graphene is lightly strengthened as E-F increases to 0.006 a.u. However, when an E-F of 0.007 a.u. is adopted, C atom moves closer to the S atom, and forming up a chemical bond between them (Fig. 6c). Besides, in this optimized structure, E<sub>ads</sub> of CO<sub>2</sub> becomes -0.25 eV and its charge increases by 0.12|e|. The Hirshfeld charge analysis further indicates that these charges are contributed by the doped system to the O atoms of CO<sub>2</sub>, bring about the dwindling of O-C-O angle (Fig. 6c). It is easy to discern the conversion of physisorption into chemisorption when the applied E-F rises from 0.006

to 0.007 a.u. When the E-F value in the range of 0.007-0.010 a.u., the  $E_{\text{ads}}$ , charge-transfer, and corresponding C–O bond length of adsorbed  $\text{CO}_2$  is further increased. At the same time, the O–C–O angle further decreases from  $161.1^\circ$  to  $140.6^\circ$ .

It should also be pointed out the binding distance from  $\text{CO}_2$  to S-decorated surface show a slight increase (Fig. 5a) when the E-F increased from 0.009 to 0.010 a.u., which phenomenon can be

attributed to the rotation of  $\text{CO}_2$  molecule (Fig. 6d). All these results indicate  $\text{CO}_2$  is efficiently captured by S-doped graphene. Particularly, the  $E_{\text{ads}}$  of  $\text{CO}_2$  under the E-F of 0.008, 0.009 and 0.010 a.u. reaches to  $-0.413$ ,  $-0.663$  and  $-0.990$  eV, respectively, which closes to the optimal range of an outstanding adsorbents for  $\text{CO}_2$  ( $-0.42$  to  $-0.82$  eV) [40]. Consequently, S-doped graphene can be considered as a promising candidate for  $\text{CO}_2$  storage, when E-F is in the scope of  $0.008 \sim 0.009$  a.u.

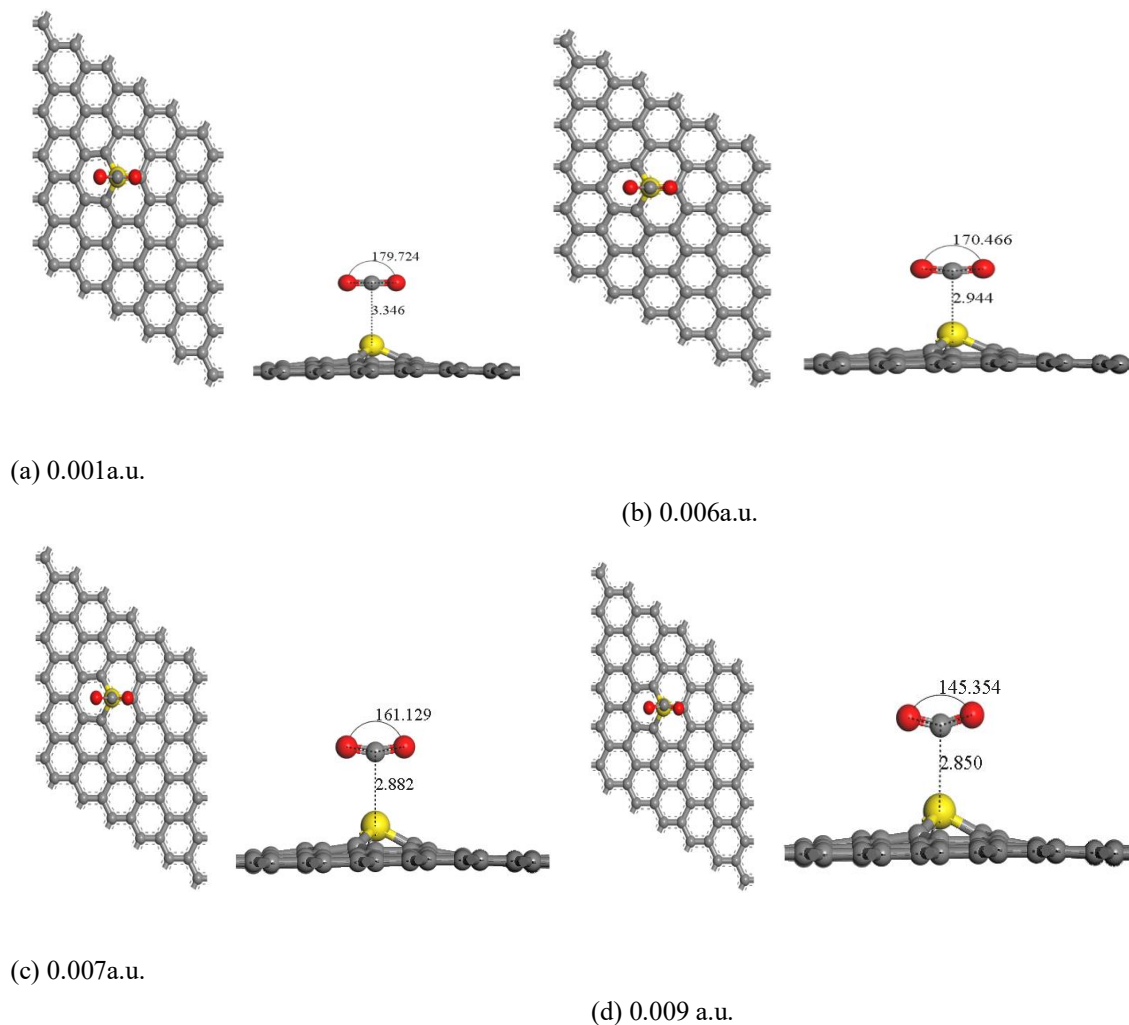


Fig. 6: Optimized configuration of  $\text{CO}_2$  over S-doped graphene under different E-F: (a)  $F = 0.001$ , (b)  $F = 0.006$ , (c)  $F = 0.007$  and (d)  $F = 0.009$  a.u.. All bond distances and angles are in Å and  $^\circ$ , respectively.

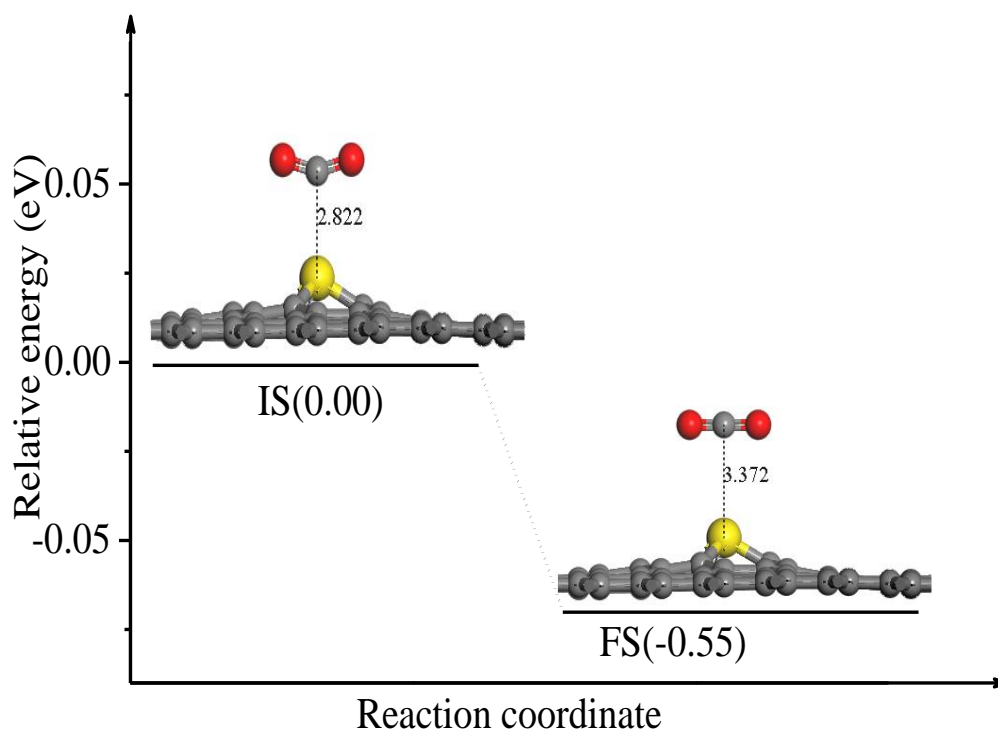


Fig. 7: The energy profile for the chemisorption to physisorption transformation of the adsorbed  $\text{CO}_2$  over S-doped graphene due to removing of the E-F ( $E\text{-F}=0.008\text{a.u.}$ ).

In addition, the release process of  $\text{CO}_2$  over S-doped graphene is also investigated by removing the applied E-F on the chemisorbed configurations. Shown in Fig. 7 is the energy change in desorption process of the chemisorbed  $\text{CO}_2$  under the E-F of 0.008 a.u. It can be found that the binding distance of  $\text{CO}_2$  and S-doped graphene changed from 2.822 to 3.372 Å by removing the E-F. Meanwhile, the  $E_{\text{ads}}$  of  $\text{CO}_2$  over S-doped graphene is reduced to  $-0.07\text{ eV}$ . These results indicate that the chemical adsorption converts to physical adsorption again when the external E-F is removed. More importantly, the desorption process of  $\text{CO}_2$  molecular is exothermic without any energy barrier.

#### $\text{CO}_2/\text{N}_2$ separation on S-doped graphene

In order to mitigate the greenhouse effect, separating  $\text{CO}_2$  from post-combustion gases ( $\text{CO}_2/\text{N}_2/\text{H}_2\text{O}$ ) is of great significance. In the 3.4 section, whether S-doped graphene can selectively capture  $\text{CO}_2$  in  $\text{CO}_2/\text{N}_2$  mixture was researched. Firstly, we investigated  $\text{N}_2$  adsorption on S-decorated graphene without an E-F. The stable structure of  $\text{N}_2$  adsorbed on S-decorated graphene without an E-F is displayed in Fig. 8(a), where the distance from  $\text{N}_2$  to

S-doped graphene is quite far with a value of 3.646 Å, and the  $E_{\text{ads}}$  is  $-0.040\text{ eV}$ , which indicates  $\text{N}_2$  is physisorbed on S-doped graphene and their interactions are weak. Similar weak interactions for  $\text{CO}_2$  and  $\text{N}_2$  adsorbed on S-decorated graphene suggest that S-decorated graphene can't applied to  $\text{CO}_2$  capturing out of  $\text{CO}_2/\text{N}_2$  mixture without the aid of E-F.

The adsorption of  $\text{N}_2$  on S-doped graphene with the E-F ranging from 0.000 a.u. to 0.010 a.u. was also studied. The final structure of  $\text{N}_2$  adsorbed on the S-doped graphene with an E-F 0.009 a.u. is presented in Fig. 8(b). Fig. 8(b) indicates that when the E-F strength is 0.009 a.u., the distance between  $\text{N}_2$  and S-doped graphene is very far with a value of 3.798 Å and the  $E_{\text{ads}}$  is 2.73 eV. The positive  $E_{\text{ads}}$  means that  $\text{N}_2$  has a very weak interaction with S-decorated graphene. This is contrast to the adsorption of  $\text{CO}_2$  on S-decorated graphene under the identical E-F (0.009a.u.), where chemical adsorption formed. The different adsorption behaviors between  $\text{CO}_2$  and  $\text{N}_2$  on S-doped graphene under identical E-F suggest that S-doped graphene may selectively capture  $\text{CO}_2$  in  $\text{CO}_2/\text{N}_2$  gas mixture with the assistance of E-F.



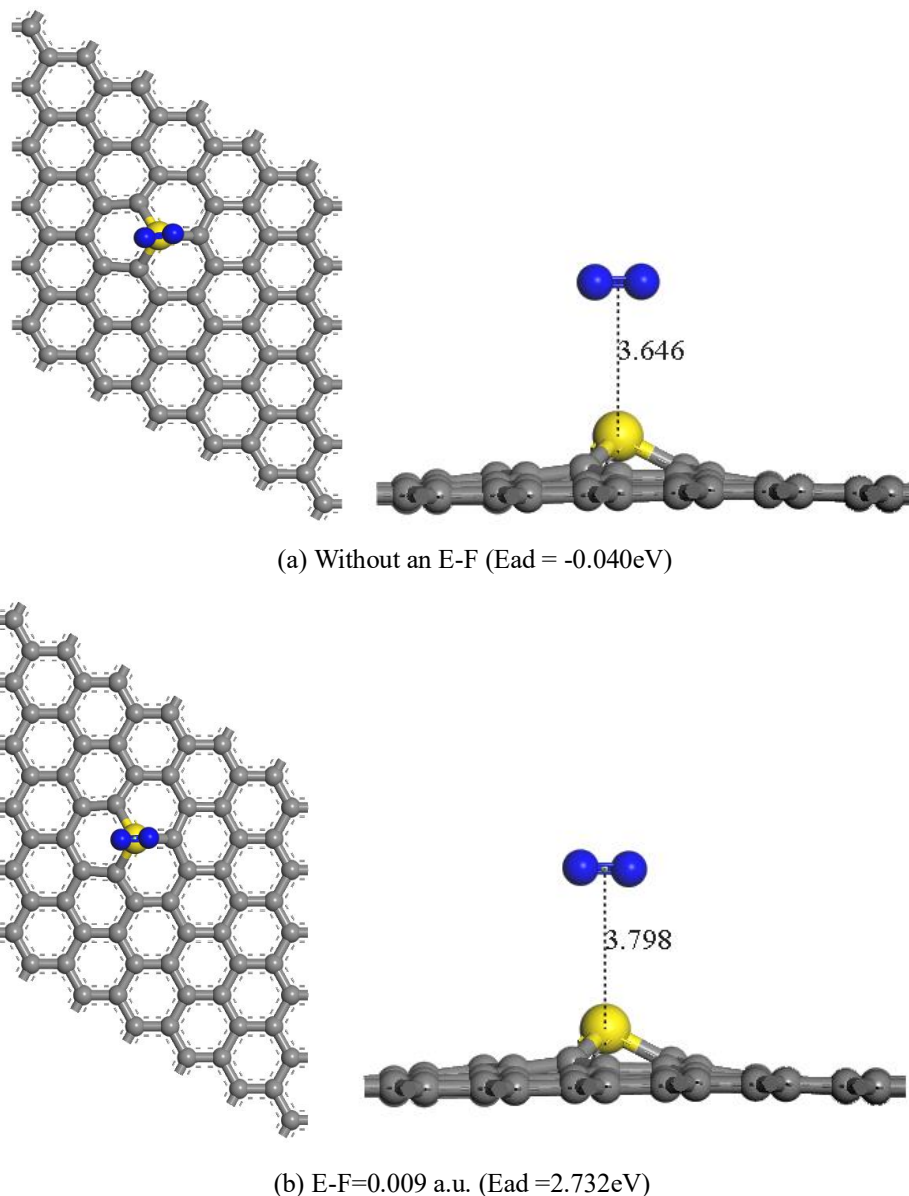


Fig. 8: Top and front views of configurations of  $\text{N}_2$  adsorption on S-doped graphene (a) without and (b) with an E-F at the strength of 0.009 a.u.

The detail about structural informations, such as distance between  $\text{N}_2$  and S-doped graphene,  $E_{ads}$  and electron transfers from S-doped graphene to  $\text{N}_2$ , in the cases of  $\text{N}_2$  adsorbed on S-decorated graphene with different E-F (0 to 0.010 a.u.) are presented in Fig. 9. As to the adsorption of  $\text{N}_2$  on S-decorated graphene with the E-F increasing from 0 to 0.010 a.u., the distances and  $E_{ads}$  between  $\text{N}_2$  and S-doped graphene are in the range of 3.646~3.815 Å and -0.040~3.275 eV, respectively (Fig. 9a). Moreover, the negligible charge transfer between  $\text{N}_2$  and S-doped graphene also

confirm the weak interaction between  $\text{N}_2$  and S-doped graphene (Fig. 9c) in all adsorbed configurations.

In addition, Fig. 9b presents the contrasts in  $E_{ads}$  of  $\text{CO}_2$  and  $\text{N}_2$  adsorbed on S-doped graphene under the E-F. The results clearly reveal that it is very easy to separate  $\text{CO}_2$  and  $\text{N}_2$  with the assistance of external E-F. All these results confirm that with the help of an applied E-F (the suitable value of E-F strength is 0.008~0.009 a.u.),  $\text{CO}_2$  can be effectively captured by S-doped graphene from the  $\text{CO}_2/\text{N}_2$  gas mixture.

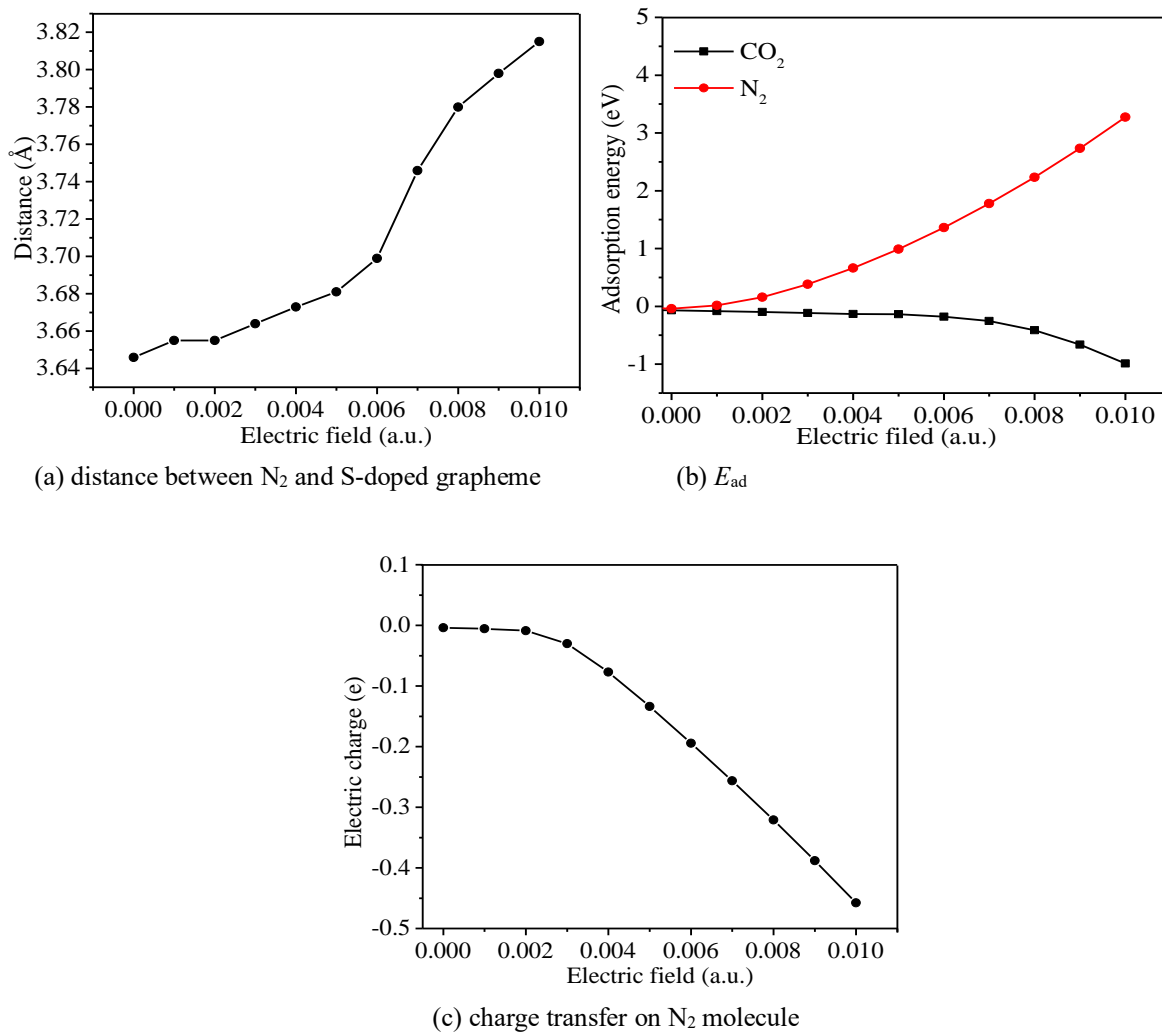


Fig. 9: The distance,  $E_{ad}$  and charge transfer between N<sub>2</sub> and S-doped graphene with different E-F.

Besides N<sub>2</sub>, H<sub>2</sub>O is another main component of flue gas. The effect of H<sub>2</sub>O on the selective adsorption of CO<sub>2</sub> by S-doped graphene was investigated and Fig. 10 shows the adsorption outcomes of H<sub>2</sub>O on S-doped graphene under different E-F. It is clearly shown that the adsorption energy increases linearly as the augmentation of E-F and have the positive value in most cases, which means that S-doped graphene interacts with H<sub>2</sub>O feebly. Moreover, the negligible charge transfer from H<sub>2</sub>O to S-decorated graphene under different E-F further confirms the weak interaction nature. All these results manifest that H<sub>2</sub>O has little effect on the capture of CO<sub>2</sub> and S-doped graphene can separate CO<sub>2</sub> in CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O gas mixture easily with the help of E-F.

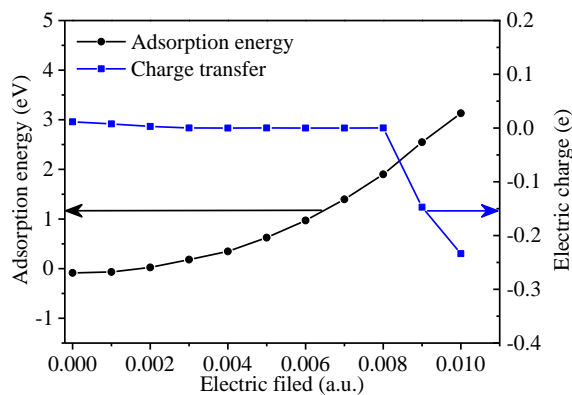


Fig. 10: The  $E_{ad}$  and charge transfer of H<sub>2</sub>O adsorption on S-doped graphene with different E-F.

## Conclusions

DFT calculations were performed on the separation and capture of CO<sub>2</sub> over S-decorated graphene from post-combustion gases (CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O). It was found that S-doped graphene could serve as an efficient CO<sub>2</sub> capture material with outstanding selectivity in CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O mixture by applying a vertical E-F ranged from 0.008 to 0.009 a.u. In detail, without E-F, CO<sub>2</sub> is physisorbed over S-doped graphene. However, by applying a vertical E-F, the adsorption properties of CO<sub>2</sub> are dramatically reinforced and the physisorption turns into a chemisorption as the E-F was 0.007 a.u. This can be attributed to the newly formed chemical bond between S atom and CO<sub>2</sub>. Moreover, CO<sub>2</sub> molecule in chemisorption state could be readily desorbed from the S-doped graphene sheet without energy barrier by removing the E-F, indicating that E-F can control the seize and free of CO<sub>2</sub>. What's more, unlike the CO<sub>2</sub>, N<sub>2</sub> (H<sub>2</sub>O) adsorbed on S-doped graphene is notably weaker as the external E-F increased. All these results suggest S-decorated graphene a promising candidate for CO<sub>2</sub> capture.

## Acknowledgements

This work was financially supported by the Doctoral Fund Project of Henan Polytechnic University (B2019-40), the Open Foundation of the State Key Laboratory of Refractories and Metallurgy (G201904), the Key Science and Technology Research Project of Henan Province (21210221589), the National Natural Science Foundation of China (52102017) and the Fundamental Research Funds for the Universities of Henan Province (NSFRF200101).

## References

1. M. Kampa, E. Castanas. Human health effects of air pollution. *Environ. Pollut.*, **151**, 362 (2008).
2. Mitchell, F. B. John. The greenhouse effect and climate change. *Rev. Geophys.*, **27**, 115 (1989).
3. D. A. Lashof, D. R. Ahuja. Relative contributions of greenhouse gas emissions to global warming. *Nature*, **344**, 529 (1990).
4. B. Liu, B. Smit. Molecular simulation studies of separation of CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, and CH<sub>4</sub>/N<sub>2</sub> by ZIFs. *J. Phys. Chem. C*, **114**, 8515 (2016).
5. K. S. Novoselov, A. K. Geim and S. V. Morozov. Two-dimensional gas of massless Dirac fermions in graphene. *Nature*, **438**, 197 (2005).
6. A. K. Geim, K. S. Novoselov. The rise of graphene. *Nat. Mater.*, **6**, 183 (2007).
7. Neto, A. H. Castro. The electronic properties of graphene. *Phys. Status Solidi*, **244**, 4106 (2010).
8. A. K. Mishra, S. Ramaprabhu. Carbon dioxide adsorption in graphenesheets. *Aip Adv.*, **1**, 321 (2011).
9. A. S. Rad, V. P. Foukolaei. Density functional study of Al-doped graphene nanostructure towards adsorption of CO, CO<sub>2</sub> and H<sub>2</sub>O. *Synthetic Met.*, **210**, 171 (2015).
10. A. A. Alghamdi, A. F. Alshahrani and N. H. Khadry. Enhanced CO<sub>2</sub> Adsorption by Nitrogen-Doped Graphene Oxide Sheets (N-GOs) Prepared by Employing Polymeric Precursors. *Materials*, **11**, 578 (2018).
11. D. Cortés-Arriagada, D. E. Ortega and N. Escobar. Fe-doped Graphene Nanosheet as an Adsorption Platform of Harmful Gas Molecules (CO, CO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>S), and the co-adsorption in O<sub>2</sub> environments. *Appl. Surf. Sci.*, **427**, 227 (2018).
12. M. D. Esrafil, L. Dinparast. A DFT study on the catalytic hydrogenation of CO<sub>2</sub> to formic acid over Ti-doped graphenenanoflake. *Chem. Phys. Lett.*, **682**, 49 (2017).
13. M. D. Esrafil, F. Sharifi and L. Dinparast. Catalytic hydrogenation of CO<sub>2</sub> over Pt- and Ni-doped graphene: A comparative DFT study. *J. Mol. Graph. Model.*, **77**, 143 (2017).
14. J. Oh, Y. H. Mo and V. D. Le. Borane-modified graphene-based materials as CO<sub>2</sub> adsorbents. *Carbon*, **79**, 450 (2014).
15. M. Wang, Z. Zhang and Y. Gong. Penta-graphene as a promising controllable CO<sub>2</sub> capture and separation material in an electric field. *Appl. Surf. Sci.*, **502**, 144067 (2020).
16. H. Guo, W. Zhang and N. Lu. CO<sub>2</sub> capture on h-BN sheet with high selectivity controlled by external electric field. *J. Phys. Chem. C*, **119**, 6912 (2015).
17. Q. Sun, G. Q. Qin and Y. Y. Ma. Electric field controlled CO<sub>2</sub> capture and CO<sub>2</sub>/N<sub>2</sub> separation on MoS<sub>2</sub> monolayers. *Nanoscale*, **9**, 19 (2017).
18. M. D. Esrafil. Electric field assisted activation of CO<sub>2</sub> over P-doped graphene: A DFT study. *J. Mol. Graph. Model.*, **90**, 192 (2019).
19. Y. Zhi, Y. Zhen and L. Guifa. Sulfur-doped graphene as an efficient metal-free cathode catalyst for oxygen reduction. *Acs. Nano.*, **6**, 205 (2012).
20. P. Hwee Ling, I. Petr and S. Zdeněk. Sulfur-doped graphene via thermal exfoliation of graphite oxide in H<sub>2</sub>S, SO<sub>2</sub>, or CS<sub>2</sub> gas. *Acs. Nano.*, **7**, 5262 (2013).
21. INAMDAR, Shaukatali and CHOI. Sulfur-containing carbon by flame synthesis as efficient

- metal-free electrocatalyst for oxygen reduction reaction. *Electrochem. Commun.*, **30**, 9 (2013).
22. W. Kiciński, M. Szala and M. Bystrzejewski. Sulfur-doped porous carbons: Synthesis and applications. *Carbon*, **68**, 1 (2014).
  23. Z. Ma, S. Dou and A. Shen. Sulfur-doped graphene derived from cycled lithium-sulfur batteries as a metal-free electrocatalyst for the oxygen reduction reaction. *Angew. Chem.*, **127**, 1908 (2015).
  24. J. Wang, R. Ma and Z. Zhou. Magnesiothermic synthesis of sulfur-doped graphene as an efficient metal-free electrocatalyst for oxygen reduction. *Sci. Rep.*, **59**, 9304 (2015).
  25. B. Delley. From molecules to solids with the DMol<sup>3</sup> approach. *J. Chem. Phys.*, **113**, 7756 (2000).
  26. J. P. Perdew, K. Burke and M. Ernzerhof. Generalized Gradient Approximation made simple. *Phys. Rev. Lett.*, **77**, 3865 (1996).
  27. J. P. Perdew, W. Ernzerhof. Accurate and simple density functional for the electronic exchange energy—Generalized Gradient Approximation. *Phys. Rev. B*, **33**, 8800 (1986).
  28. B. Delley. Hardness conserving semilocal pseudopotentials. *Phys. Rev. B*, **66**, 155125 (2002).
  29. S. Grimme. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.*, **27**, 1787 (2006).
  30. S. Grimme. Accurate description of van der Waals complexes by density functional theory including empirical corrections [J]. *Journal of Computational Chemistry*, **25**, 1463 (2004).
  31. N. A. Benedek, I. K. Snook and K. Latham. Application of numerical basis sets to hydrogen bonded systems: A density functional theory study. *J. Chem. Phys.*, **122**, 144102 (2005).
  32. Y. Inada, H. Orita. Efficiency of numerical basis sets for predicting the binding energies of hydrogen bonded complexes: Evidence of small basis set superposition error compared to Gaussian basis sets. *J. Comput. Chem.*, **29**, 225 (2008).
  33. J. Wang, Z. Huang, L. Lu, et al. Colloidal Co single-atom catalyst: a facile synthesis strategy and high catalytic activity for hydrogen generation. *Green Chem.*, **22**, 1269 (2020).
  34. J. D. Pack, H. J. Monkhorst. "Special points for Brillouin-zone integrations"---a reply. *Phys. Rev. B*, **16**, 1748 (1977).
  35. F. L. Hirshfeld. Bonded-atom fragments for describing molecular charge densities. *Theor. Chem. Acc.*, **44**, 129 (1977).
  36. D. R. Cooper, B. D'Anjou and N. Ghattamaneni. Experimental review of graphene. *Isrn. Cond. Mat. Phys.*, **2012**, 1 (2014).
  37. J.W. Feng, Y. J. Liu and H. X. Wang. Gas adsorption on silicene: A theoretical study. *Comput. Mater. Sci.*, **87**, 218 (2014).
  38. X. Fan, W. T. Zheng and J. L. Kuo. Oxygen reduction reaction on active sites of heteroatom-doped graphene. *Rsc. Adv.*, **3**, 5498 (2013).
  39. Y. Tang, Z. Yang and X. Dai. Formation, stabilities, and electronic and catalytic performance of platinum catalyst supported on non-metal-doped graphene. *J. Phys. Chem. C.*, **117**, 5258 (2013).
  40. S. Chu, A. Majumdar. Opportunities and challenges for a sustainable energy future. *Nature*, **488**, 294 (2012).