

DFT study of carbon dioxide capture on functionalized graphane sheets

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Abstract— CO₂ capture and storage is a potential means to alleviate global warming and ocean acidification. Herein, CO₂ capture with various functionalized graphanes and the effects of functional groups are investigated by density functional theory (DFT). Our results show that CO₂ adsorbs weakly on a bare graphane sheet, and absorbs slightly better when functionalized with P-substituted graphane, and increasingly better with PH₂-grafted on H atoms. Further, the presence of H₂O would provide strong CO₂ adsorption and the exothermic adsorption energies could reach about -42 kJ/mol with PH₂-grafted on graphane. This computational work provides an atomic-level strategy in the design of functionalized graphane and carbon-based adsorbent materials for CO₂ capture and storage.

Keywords—DFT, CO₂ capture, Graphane, Functional groups

I. Introduction

The concentration of greenhouse gas carbon dioxide (CO₂) in the atmosphere has risen from about 310 to 390 ppm over the past few decades, and the pH value of surface seawater would decrease from 8.2 to 7.8 by 2095 for the accumulation effect of dissolved CO₂.^[1] Carbon capture and storage (CCS) is a promising approach to capture waste CO₂ from large point sources, such as fossil fuel power plants, and has attracted considerable attention during the past several years. CCS transports CO₂ to a storage site, or deposits it to, for example, an underground geological formation to avoid it entering the atmosphere.^[2] CO₂ capture and separation at stationary point source is very important for practical CCS applications.^[3] So, one of the key issues to improve CO₂ capture performance is to explore efficient capture materials, which should have high CO₂ adsorption capacity, excellent adsorption selectivity, and good chemical and mechanical stability.^[4] Various adsorbent materials have been proposed for CO₂ capture. They include carbon nanotubes,^[5-8] activated carbon,^[9] porous organic polymers,^[10,11] covalent organic frameworks,^[12,13] metal organic frameworks,^[14] nanoporous carbons,^[15] porous graphane membranes,^[16] and Zeolites.^[17,18] However, due to their physical characteristics or economic consideration in the processes of synthesis, manufacture and regeneration, they are not fully desirable. Therefore, the development of feasible materials to enhance CO₂ capture and separation is still outstanding.

Graphane, a lengthened two-dimensional (2-D) polymer of hydrocarbon, is a burgeoning carbon-based material with attractive properties.^[19] Graphane is composed of a monolayer of 2-D sheets of carbon atoms, and the carbon bonds of graphane are in sp³ configuration, as opposed to graphene's sp² bond configuration.^[20,21] Unlike graphene, hydrogen grafted to a carbon atom on graphane sheet can be substituted by functionalities without affecting the remaining parts of the graphane structure.^[22] Maximized atomic utilization and tunable composition and functionalities of graphane^[23,24] offer new possibilities for structure of materials based on two-dimensional carbon for applications including adsorption and catalysis. Xiao *et al.*^[22] investigated CO₂ adsorption thermodynamics over N-substituted/grafted graphanes using DFT. As Phosphorus is a congener of nitrogen, and P-doped graphane is postulated to be a high-temperature superconductor with a T_c above 90 K, based on the BCS theory,^[25] this material is thought to have special absorption properties. However, P-doped graphane as adsorbent material has not been investigated.

In this paper, we present a DFT investigation of CO₂ adsorption over P-substituted/grafted graphanes. CO₂ adsorption energies over graphanes with or without P-functionalization are compared to identify the effects of P-site density and position. The effect of moisture addition is also explored. The partial density of states (PDOS) analysis is preformed to elucidate the CO₂ adsorption rule. This work therefore contributes to the fundamental understanding of the structural, energetic, and electric properties of substituted/grafted graphanes for CO₂ adsorption and may be useful for the design and screening of adsorbent materials for carbon capture and storage.

II. Computational details

DFT calculations were performed with the DMol³ program package in Materials Studio 7.0 of Accelrys Inc., using the exchange-correlation functional of GGA-PW91 approximation. A vacuum layer of 15 Å was added perpendicular to the single layer surface. A (3 × 3 × 1) Monkhorst-Pack (MP)^[26] *k*-point mesh was used for all of the surfaces. The system was modeled as a 4 × 4 supercell of graphane, which contained 32 C atoms plus 32 H atoms, as shown in Fig. 3.1a. The unit cell of graphane was initially optimized as a = b = 2.46 Å, which is close to the reported unit cell values of graphane (a = b = 2.52 Å).^[21] The atomistic models of graphane was built as chair conformation as it is more stable than the boat configuration.^[21] The isolated gas phase adsorbates (CO₂ and H₂O) were optimized separately. All the atoms in the cell were relaxed and all calculations were spin-polarized.

The adsorption energy (E_a) is calculated by subtracting the sum of the energy of the isolated adsorbent surface and the energy of the optimized gas-phase adsorbate from the energy of the optimized adsorbate-adsorbent system, which can be expressed by the following equations:

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$$E_a = E_{\text{adsorbent-adsorbent}} - E_{\text{adsorbent}} - E_{\text{gas}} \quad (1)$$

where $E_{\text{adsorbent}}$ is the energy of the bare or functionalized graphene adsorbent, E_{gas} is the energy of isolated CO_2 or H_2O , $E_{\text{adsorbent-adsorbent}}$ is the total energy of the adsorbent-adsorbent system, such as the adsorbent- CO_2 , the adsorbent- H_2O , and the adsorbent- $(\text{CO}_2+\text{H}_2\text{O})$ system. A more negative E_a indicates a stronger adsorption.

III. Results and discussion

A. CO_2 adsorption over P-Substituted and PH_2 -grafted graphanes

The optimized basic graphene surfaces (a) bare, (b) P-substituted, and (c) PH_2 -grafted are shown in Fig. 1. The substitution of a single C atom in the lattice with a P atom led to P concentration of 3.13 wt %. As shown in Fig. 1a, the bare graphene structure is in a chairlike conformation with the H atoms alternating on both sides of the plane, which is a preferable conformation compared to the boatlike conformer with the H atoms alternating in pairs.^[21,22] All the C atoms form a hexagonal network, and the calculated C-C bond length is 1.50 Å, similar to the sp^3 bond length of 1.53 Å of ethane, and much longer than the typical bond length (1.42 Å) of sp^2 carbon. As shown in Figs. 1b and 1c, the basic graphene structure is well retained with slight distortion of the hexagonal lattice in both P-substituted and PH_2 -grafted structures.

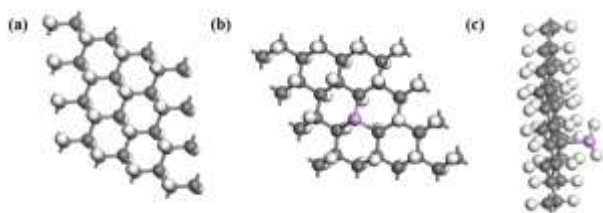


Fig. 1. Optimized graphene surfaces: (a) bare, (b) P-substituted, and (c) PH_2 -grafted. Color code: gray, C; purple, P; white, H.

CO_2 adsorption over P-substituted graphanes. To study the effects of P-site density on P-substituted graphene on CO_2 adsorption, CO_2 adsorption thermodynamics over a 4×4 graphene unit cell surface with 0 ~ 2 units of P-sites (0, 3.13, and 6.27 wt% of P-site density) were studied. The optimized interaction configurations and adsorption energies are given in Fig. 2. For the substitution of 2 P-sites per graphene cell, three configurations of P-sites in meta-, para-, and ortho-positions were considered. Doping P atoms into a graphene unit cell strengthens the CO_2 adsorption when compared to adsorption on an undoped surface (adsorption energy changes from -3.313 (undoped) to -4.895 (1-P) and -9.861 (2-P ortho-position) kJ/mol, respectively). The result suggests that higher P-site density gives more exothermic CO_2 adsorption. With 2 P atoms doped in the graphene unit cell, the CO_2 adsorption energy varies with the placement of the P atoms, which increases in the order of ortho > para > meta. Regardless of the concentration of P-doped, all the adsorption of CO_2 over P-substituted graphene is weak, similar to CO_2 adsorption over N-substituted graphene.^[22]

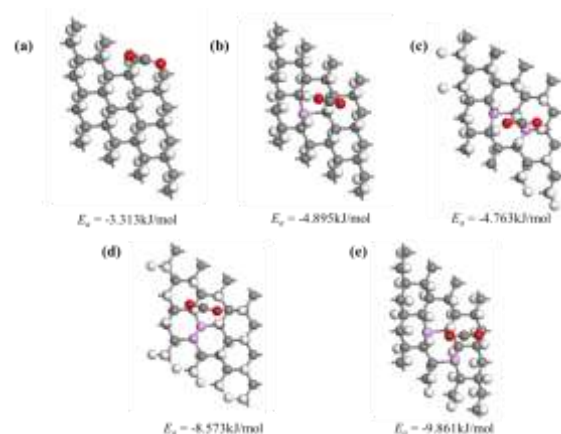


Fig. 2. Optimized interaction configurations and adsorption energies (E_a , in kJ/mol) for CO_2 adsorption over graphanes: (a) bare graphene; (b) single P-substituted graphene; (c) 2 P-substitutions in meta-position; (d) 2 P-substitutions in para-position; (e) 2 P-substitutions in ortho-position. Color code: gray, C; red, O; purple, P; white, H.

CO_2 adsorption over PH_2 -grafted graphanes. Primary phosphino (PH_2 -) grafted graphanes are expected to offer stronger basicity,^[27] leading to a stronger CO_2 adsorption (an acidic molecule). This hypothesis was investigated via studying several modes of adsorption on these surfaces. One interaction configuration was CO_2 physisorption, the other hypothesis configuration was the reaction of PH_2 - and CO_2 .^[28] Figs. 3a and 3b show the proposed interaction configurations and adsorption energies. CO_2 adsorbs weakly on graphene surface-functionalized with single grafted PH_2 -sites, with an exothermic adsorption energy -6.762 kJ/mol. The reaction of PH_2 - and CO_2 (Fig. 3b, $E_a = 42.997$ kJ/mol) is not favorable, comparing with physisorption over a single PH_2 -functionalized surface.

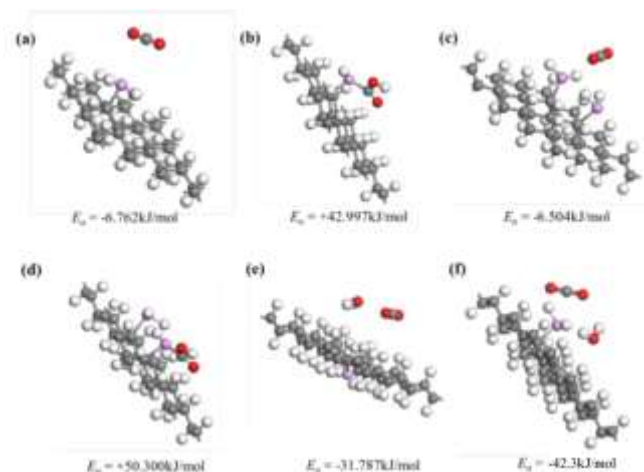


Fig. 3. Proposed interaction configurations and adsorption energies (E_a , in kJ/mol) for CO_2 adsorption on P-functionalized graphanes: (a) PH_2 -grafted by physisorption; (b) PH_2 - reaction with CO_2 ; (c) 2PH_2 -grafted by physisorption; (d) one of the 2PH_2 - reacting with CO_2 ; (e) P-substituted with H_2O ; (f) PH_2 -grafted with water. Color code: gray, C; red, O; purple, P; white, H.

To further survey the effect of $-\text{PH}_2$ functional group on CO_2 adsorption, a second $-\text{PH}_2$ functional group proximate to the $-\text{PH}_2$ site is added. Also, two interaction configurations were studied: CO_2 adsorption by (a)

physisorption, (b) one of the 2PH_2 - reaction with CO_2 . The optimized interaction configurations and adsorption energies are shown in Figs. 3c and 3d. Physisorption occurs with an adsorption energy of -6.504 kJ/mol, while adsorption energies for PH_2 - reaction with CO_2 were also positive. The positive values of E_a in two reaction configurations indicate that the structures are unstable relative to desorption. Bending the CO_2 molecule or transferring a H atom to CO_2 creates a local minimum energy structure, thus forming the instability.^[22] Compared to one $-\text{PH}_2$ grafted, two proximate $-\text{PH}_2$ functional groups on graphane hinder the CO_2 adsorption, which is probably due to the geometrical restrictions. Overall, similar to P-substituted graphane, the density of phosphorus sites only slightly affects the CO_2 adsorption energy. The adsorption of CO_2 over PH_2 -grafted graphane is relatively weak, and PH_2 - reaction with CO_2 is not favorable. Therefore, neither P-substitution nor directly grafted PH_2 -groups on graphane provide favorable sites for CO_2 adsorption.

B. CO_2 adsorption over P-Substituted and PH_2 -grafted graphanes in presence of H_2O

The content of water is 8-20% in power station off-gas,^[29] so the effect of H_2O on CO_2 adsorption should be taken into consideration. Figs. 3e and 3f show the proposed interaction configuration and adsorption energies for CO_2 adsorption over P-substituted/directly grafted PH_2 -graphanes in the presence of H_2O . In Fig. 3e, the H_2O molecule is weakly bonded to the P-site, and the measured OH–P bond distance is 5.155 Å. The water molecule adsorbs CO_2 strongly through a C–O water electrostatic interaction, as reflected by the adsorption energy E_a of -31.787 kJ/mol. In Fig. 3f, CO_2 adsorption to PH_2 -grafted graphane with H_2O , the H_2O molecule is bonded to the PH_2 group with the OH–P bond distance 2.507 Å, with E_a of -42.3 kJ/mol. The presence of H_2O strongly enhances CO_2 adsorption over both P-substituted and PH_2 -grafted graphanes. This result shows that as water is present in the flue gas^[29], and the process can be completed without the introduction of additional water, the extraction of CO_2 from power station exhaust gas would be viable. However, the presence of water leads to an impure CO_2 stream upon desorption, which needs to be further dried.^[22] Our results of CO_2 adsorption over P-substituted/directly grafted PH_2 -graphanes in the presence of H_2O are also similar to N-substituted/directly grafted NH_2 -graphanes^[22].

To better understand the change in the electronic structure of the gas adsorption system with the presence of water, the electron density for $\text{CO}_2+\text{H}_2\text{O}+\text{GAPH}_2$ adsorption system was analyzed. The results are shown in Fig. 4. It can

be seen that there is no electron distribution among the CO_2 molecule, the H_2O molecule and the GAPH_2 sheet. This indicates that the adsorption is physical. Also, the partial density of states (PDOS) of P-substituted/ PH_2 -grafted, CO_2 on $\text{GAP}+\text{CO}_2+\text{H}_2\text{O}$ and $\text{GAPH}_2+\text{CO}_2+\text{H}_2\text{O}$ adsorption system were analyzed, respectively. Fig. 5a shows the PDOS for P-substituted configuration in $\text{GAP}+\text{CO}_2+\text{H}_2\text{O}$ adsorption system. There is no obvious change around the Fermi level. However, the p orbital has slight change after adsorption. This may be caused by the transfer between some electrons. Fig. 5b illustrates that the significant PDOS difference for CO_2 in the adsorption system may also be caused by electrons transferring. Then, in Fig. 5c, the PDOS reveals the change of PH_2 -grafted in $\text{GAPH}_2+\text{CO}_2+\text{H}_2\text{O}$ adsorption system. There exists mild shift of both s and p orbitals. The change of CO_2 in $\text{GAPH}_2+\text{CO}_2+\text{H}_2\text{O}$ system is similar with $\text{GAP}+\text{CO}_2+\text{H}_2\text{O}$. The large charge transfer is expected to induce the change.

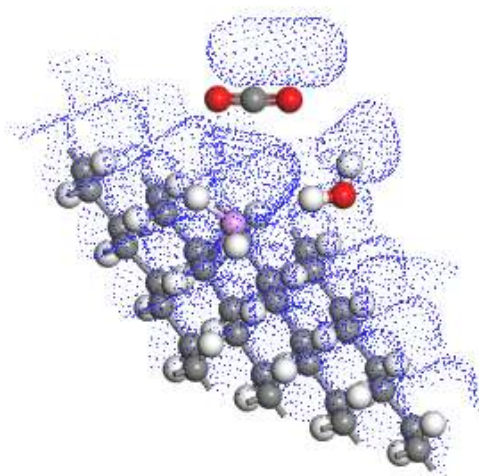


Fig. 4. The electron density for $\text{CO}_2+\text{H}_2\text{O}+\text{GAPH}_2$ adsorption system.

IV. Conclusions

CO_2 adsorption over various types of P-substituted/grafted graphanes was studied using DFT. P-substituted/grafted graphanes were constructed by substitution of lattice carbon or surface hydrogen with P-functional groups. CO_2 adsorbs weakly on a graphane surface functionalized with single substituted P- or grafted PH_2 -sites. The adsorption of P-substituted/grafted graphanes can be strengthened with the presence of co-adsorbed H_2O . This theoretical work provides an atomic-level strategy in the design of functionalized graphane and carbon-based adsorbent materials for CO_2 capture and storage.

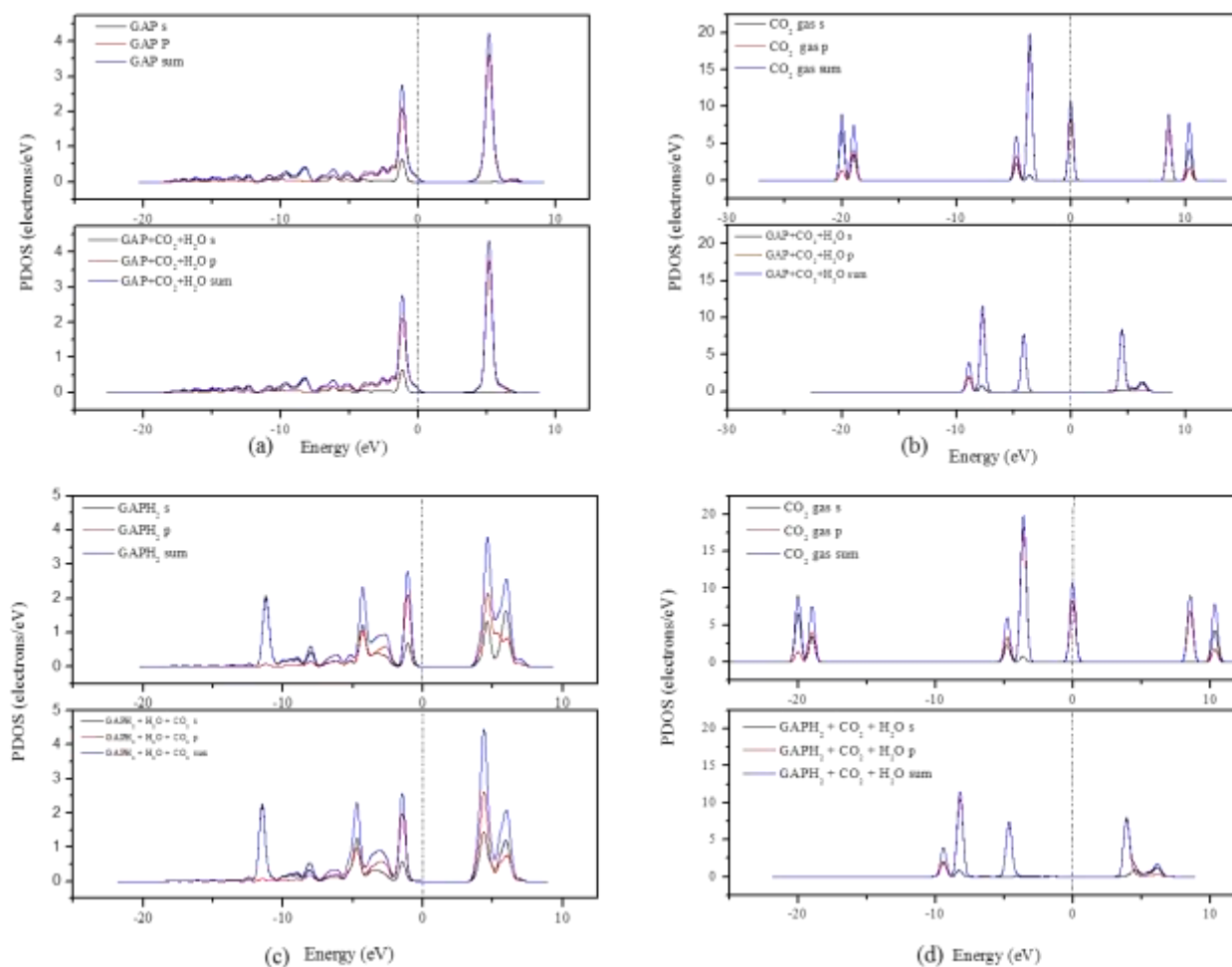


Fig. 5. Partial density of state (PDOS) for GAP+CO₂+H₂O and GAPH₂+CO₂+H₂O systems (a) PDOS of P in GAP+CO₂+H₂O; (b) PDOS of CO₂ in CO₂+H₂O+GAPH₂; (c) PDOS of PH₂ in GAPH₂+CO₂+H₂O; (d) PDOS of CO₂ in GAPH₂+CO₂+H₂O.

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