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Adsorption behavior of CO_2 on pristine and doped phosphorenes: A dispersion corrected DFT study

Hong-ping Zhang[a,d,*], Aijun Du[b], Quan-bin Shi[c], Yanfang Zhou[a], Yaping Zhang[a], Youhong Tang[d,*]

[a] State Key Laboratory of Environmental Friendly Energy Materials, Engineering Research Center of Biomass Materials, Ministry of Education, School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang, Sichuan 621010, China
[b] School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Queensland 4001, Australia
[c] School of Environmental Science and Engineering, Tianjin University, Tianjin 300350, China
[d] Centre for NanoScale Science and Technology and College of Science and Engineering, Flinders University, South Australia 5042, Australia

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ABSTRACT

The density functional theory (DFT) method was used to study the adsorption of CO_2 molecules on pristine and doped phosphorenes. Twenty dopants were considered during this study: Fe, Co, Ni, Ti, Cu, Au, Ag, Ca, Cr, Pd, Pt, V, Sr, Mn, B, C, N, O, Si, Ge, Se, and S. Two initial configurations of CO_2 on the pristine and doped phosphorenes were also studied. The results for adsorption energy, isosurface of electron density difference, partial density of states, and charge transferring analysis indicated that pristine phosphorene had a very weak interaction with CO_2. Some of transition metallic dopants, namely Fe, Co, Ti, Ni, Cr, and V, significantly improved the interactions between phosphorenes and CO_2. Some other metallic dopants, however, namely Au, Ag, Pd, and Pt, and nonmetallic dopants, namely Ge, Si, Se, S, N, C, B, and O had negligible effect on the interactions between CO_2 and phosphorene. Cr, Fe, Ti and V-doped phosphorenes had the potential to enhance CO_2 adsorption with a particular CO_2 configuration. The role of charge donor or acceptor changed between CO_2 and (V- Cr-, Fe-, and Ti-) doped phosphorenes when the initial CO_2 configuration changed. Thus, the use of transition metallic dopants was an effective way to enhance the interactions between CO_2 and phosphorene. In particular, (V- Cr-, Fe-, and Ti-) doped phosphorenes showed the potential to sense or capture CO_2 molecules.

1. Introduction

Mitigation of carbon dioxide emissions is a pressing concern due to the close relationship between carbon dioxide and global climate change. The key issues in the general route to mitigating carbon dioxide emissions can be classified into two aspects: (a) carbon dioxide capture and storage can be very effective for alleviating the pressure of carbon dioxide emissions and (b) conversion of carbon dioxide into fuel is very meaningful for reducing carbon dioxide emission and for the production of renewable energy. Nevertheless, the capture and storage of carbon dioxide is the foundation of its advanced treatment and conversion. Currently, the best-known commercial technology for effective CO_2 capture utilizes conventional absorber/stripper systems [1]. However, energy consumption, corrosion of equipment, and high consumption of liquid amino limit this technology. Thus, exploration of novel materials with sorption properties tailored for CO_2 can be very meaningful, with the potential for providing another strategy for alleviating CO_2 emissions.

Several kinds of adsorbent have been explored for use in CO_2 capture and storage [2–10]. Various porous sorbents including metal-organic frameworks (MOFs) [2,3], zeolites [4,5], and polymers [6–8] have been studied as candidates for CO_2 capture. Yaghi et al. [2] demonstrated that MOF-177 exhibited outstanding CO_2 capture ability at low pressures compared to other MOFs and zeolite 13X. Jones et al. [8] proposed a novel hybrid adsorbent based on poly (L-lysine) and mesoporous silica that had excellent CO_2 capture ability among amino-based adsorbents. Long et al. [9] reviewed CO_2 captured by metal-organic frameworks, investigating adsorption behavior and current research. CaO-based sorbents for CO_2 derived from eggshell and red muds were studied by He et al. [10].

Graphene, the classical representative of 2D nanomaterials, has attracted much research interest by virtue of its outstanding properties [11]. Among its applications, graphene is regarded as a promising substrate for gas adsorption and storage due to its maximized atomic utilization ratio (large specific surface area) and adjustable composition [12,13]. Xiao et al. [13] studied the effect of nitrogen on the capture ability of graphene on CO_2 by the DFT method and found that CO_2 adsorbed weakly on a graphene surface functionalized with a single,

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* Corresponding authors at: Centre for NanoScale Science and Technology and College of Science and Engineering, Flinders University, South Australia 5042, Australia.
E-mail addresses: zhp1006@126.com (H.-p. Zhang), youhong.tang@flinders.edu.au (Y. Tang).

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isolated substituted N- or grafted NH_2-sites. The presence of co-adsorbed H_2O on the graphene could promote CO_2 adsorption on both N- and NH_2-sites. Phosphorene, the monolayer form of phosphorus, was recently exfoliated from its bulk. It is regarded as another interesting elemental 2D material that has better performance as semiconductor than graphene due to its direct band gap [14,15]. Chemical sensing devices based on phosphorene were reported theoretically and experimentally [16–22]. Zhou et al. [16] reported the chemical sensing of nitrogen dioxide (NO_2) using field-effect transistors based on multilayer black phosphorus. Cui et al. [17] reported a similar study of phosphorene-nanosheet-based field-effect transistors for NO_2 sensing. Kuang et al. [18] studied the adsorption behavior of acidic gases (CO_2, NO_2, and SO_2) on Li-, Al-, Ni-, and Pt-doped phosphorenes. Their study indicated that Li- and Al-doped phosphorenes were promising adsorbents for CO_2 capture. The adsorption of small gas molecules of CO, H_2O, CH_4, and NH_3 on black phosphorene was investigated by Zhang et al. [22] using the DFT method. These theoretical and experimental studies demonstrated the promising application of phosphorene as a gas sensor and for gas capture.

Element doping is an effective way to alter the gas capture ability of 2D materials. To explore the effect of doping on the interactions between phosphorene and CO_2, several kinds of elements should be investigated. DFT studies of CO_2 adsorption behaviors on various materials have been conducted, with the aim of exploring the effects of CO_2 adsorbents [23–27]. The effects of external electric fields on the interactions between CO_2 and MoS_2 were investigated by Sun et al. [23] using the DFT method. They reported that electric fields could help to separate CO_2 and N_2 on the MoS_2 surface. Cu vacancies were found to be more important than oxygen vacancies for adjusting the interactions between CO_2 and Cu_2O (111) [24]. The interactions between CO_2 and MgO film were studied by Tosoni et al. using the DFT method [25]. The authors concluded that the ultrathin MgO film could play the role of a catalytic material. Fe (111) was considered by Chen et al. [26] to show excellent catalytic activity on CO_2. Ko et al. [27] utilized the DFT method to explore the interactions between CO_2 and a bimetallic alloy surface.

Although the interactions between CO_2 and various materials have been studied by the DFT method, including CO_2-phosphorene systems [18,22], no systematic study of the effects of dopants on the interactions between CO_2 and phosphorene has been reported. In this study, DFT calculations were used to examine CO_2 adsorption over various types of doped phosphorene. A series of DFT models was used to identify the possible doping modes of doped phosphorene. Two different classical initial configurations of CO_2 on doped phosphorene were considered. Partial density of states, isosurface of electron density difference, and charge transfer were analyzed to investigate the different roles of types of dopants on the interactions between CO_2 and phosphorene. The poor prediction performance of the conventional density functional theory on the CO_2 adsorption thermodynamic has been reported [28], because it does not account for the long-range van der Waals interactions which has been extensively believed to have a significant impact on the energetics and structure of these systems. Thus, during our calculations, dispersion corrections were considered.

2. Computational methods

2.1. Simulation parameters

The DFT program Dmol^3 in Materials Studio (Biovia, San Diego, CA), in which physical wave functions are expanded in terms of numerical basis sets, was used for all the calculations in this study. Dmol^3 produces highly accurate results while keeping computational cost low [29–31]. The double numerical basis set with polarization function (DNP), that is comparable to the 6-31G** basis set, was utilized during the simulation. The core electrons were treated with DFT semicore pseudopotentials. The exchange-correlation energy was calculated using the Perdew-Burke-Ernzerhof generalized gradient approximation [32]. Special point sampling integration over the Brillouin zone was employed using the Monkhorst-Pack schemes with a 6 × 6 × 1 k-point mesh [33]. A Fermi smearing of 0.005 Ha (1 Ha = 27.21 eV) and a global orbital cutoff of 7 Å were employed. The convergence criteria for the geometric optimization and energy calculation were set as follows: (1) a self-consistent field tolerance of 1.0×10^{-6} Ha/atom, (2) energy tolerance of 1.0×10^{-5} Ha/atom, (3) maximum force tolerance of 0.002 Ha/Å, and (4) maximum displacement tolerance of 0.005 Å. Spin polarized calculations were performed during all the calculations.

Table 1
Binding energy values between dopants and phosphorene, distances between dopants and phosphorus atoms in different doped phosphorene systems.

Dopants	Site	E_{bin} (eV)	E_{bin} (Ref) (eV)	d (D-P) (Å)	d (D-P) (Ref) (Å)
B	H	−5.153	–	1.912	–
C	B	−5.635	–	1.693	–
N	B	−4.549	–	1.626	–
O	T	−5.298	−2.06	1.516	1.50
S	T	−2.976	–	1.967	–
Se	T	−2.264	–	2.118	–
Cu	H	−2.792	−2.18	2.230	2.23
Ag	H	−1.618	−1.13	2.450	2.45
Au	H	−1.788	−1.61	2.370	2.37
Ca	H	−2.817	–	2.740	
Ti	H	−3.820	−3.41	2.387	2.40
V	H	−3.475	−2.68	2.317	2.39
Cr	H	−1.551	−1.66	2.374	2.39
Fe	H	−3.684	−2.70	2.146	2.18
Co	H	−4.279	−3.56	2.09	2.13
Ni	H	−4.368	−4.09	2.11	2.12
Pd	H	−3.40	−3.48	2.28	2.27
Pt	H	−4.551	−4.71	2.23	2.23

Various doped phosphorene models were built based on the DFT optimized phosphorene model. Three doping sites were considered: H site above P6 hexagon, B site above the mid-point of the P—P bond, and T site on top of the P atom. To find the equilibrium doping configurations, all the dopant-phosphorene systems were optimized by the DFT method. The optimized doped phosphorene models are shown in Fig. 2. The bond lengths of P—P or dopant-P are listed in Table 1. Comparison of our calculation results with the reports of others demonstrated that our optimized models agreed well with their findings [34–36]. The optimized stable doping sites of different dopants can be found in Table 1. After investigation of the different doping behaviors of dopants on phosphorene, the adsorption behaviors of CO_2 on pristine and doped phosphorene were explored by considering two different initial CO_2 configurations. The first was the oxygen atom of CO_2 pointing to the phosphorene surface; the other was the main axis of CO_2 that was parallel to the phosphorene surface.

The binding energy (E_{bin}), indicating the intensity of interaction between CO_2 molecule and phosphorene surfaces, was derived according to Eq. (1):

$$E_{bin} = E_{phosphorene+CO_2} - E_{CO_2} - E_{phosphorene} \tag{1}$$

where $E_{phosphorene+CO_2}$, $E_{phosphorene}$, and E_{CO_2} represent the total energy of the interaction system, the energy of phosphorene, and the energy of CO_2 molecule, respectively. A negative E_{bin} corresponds to a stable adsorption and a more negative E_{bin} results in a more stable adsorption system. The electron density difference was very effective for studying the change in electron density during CO_2 adsorption, which was calculated by subtracting the electron density of the isolated CO_2 molecule (ρ_{CO_2}) and the phosphorene surface ($\rho_{phosphorene}$) from the total electron density of the system ($\rho_{phosphorene+CO_2}$), as shown in Eq. (2).

$$\Delta\rho = \rho_{phosphorene+CO_2} - \rho_{CO_2} - \rho_{phosphorene} \tag{2}$$

Partial density of states (PDOS) analysis can be a useful method of exploring the interactions between CO_2 molecules and phosphorene at