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1 **Promoting sensitivity and selectivity of HCHO sensor based**
2 **on strained InP₃ monolayer: A DFT study**

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15

16

1 **Abstract**

2 Sensitive materials for formaldehyde (HCHO) sensor need high sensitivity and
3 selectivity. The research on two dimensional (2D) sensitive material is growing, and
4 most studies focus on the pristine or modified graphene. So it is essential to introduce
5 other 2D materials into HCHO gas sensor. In this report, the adsorption behaviors of
6 organic gas molecules including C₂H₆, C₂H₄, C₂H₂, C₆H₆, C₂H₅OH and HCHO over
7 indium triphosphide (InP₃) monolayer were studied by using first-principle atomistic
8 simulations. The calculation results demonstrate that InP₃ monolayer has a high
9 sensitivity and selectivity to HCHO than others. By comparing the structures and
10 adsorption results of InP₃ monolayer, graphene and single-layered MoS₂, it was found
11 that the polarity bonds and steric effect of the site on monolayer play an important
12 role in the detection of HCHO. The effect of strain on the gas/substrate adsorption
13 systems was also studied, implying that the strained InP₃ monolayer could enhance the
14 sensitivity and selectivity to HCHO. This study provides useful insights into the
15 gas-surface interaction that may assist future experimental development of 2D
16 material for HCHO sensing and performance optimization based on strain.

17 **Keywords:** First-principles calculation; HCHO sensing; InP₃ monolayer; strain

18

1 **1 Introduction**

2 Formaldehyde (HCHO) is one of the most harmful volatile organic
3 compounds (VOCs), and is usually discharged from many products that are
4 widely used in the world [1]. Long exposure to the air containing a certain
5 amount of HCHO may cause harmful impacts on human health. To quickly and
6 accurately detect HCHO, both sensitive material and sensing mechanism are
7 necessary to be developed and a lot of efforts had been made in this research
8 field [2-4]. From the point of view of sensitive material, a series of metal oxide
9 semiconductors have been reported, such as TiO₂, ZnO, SnO₂, In₂O₃ and so on
10 [3, 5, 6]. The investigations on innovative chemical materials have also brought
11 metal-organic frameworks [7] and carbon nanotube [8] into such a research
12 field. Although these materials have the ability of HCHO detecting, they still
13 have some limitations such as low relative resistance changes, low selectivity
14 and long-term instability and so on. Thus, the study on the sensitive materials to
15 HCHO will never stop.

16 The discovery of graphene has shed a new light on the investigation of the
17 sensitive material for HCHO detecting, for its ultra-thin structure, huge specific
18 surface area, high conductivity and low electrical noise [9-11]. The
19 two-dimensional (2D) materials with large surface area are believed can be
20 fully in contact with the gas, and more conducive to enhance the performance
21 of the gas sensor. Regrettably, the interaction between graphene and HCHO
22 was found to be pretty weak [12, 13], which may limit the further enhancement

1 of the graphene-based sensor performance. To solve this problem, some efforts
2 have been made by compositing graphene with metal oxide or metal
3 nanoparticles [13, 14]. However, it seems that the related research is limited in
4 pristine or modified graphene. The family of 2D material is growing rapidly in
5 recent years, including silicone [15], germanane [16], phosphorus allotropes [17,
6 18], MXenes, and transition-metal dichalcogenides (TMDs) [19, 20]. Therefore,
7 extending the research to other 2D materials is a promising way and may help
8 us find a more sensitive material for HCHO detecting.

9 The recently predicted InP_3 monolayer [21] is a new category of layered
10 indirect-band gap semiconductor, which has been theoretically discovered by Miao *et*
11 *al.* and expected to be fabricated experimentally from its layered bulk crystal by
12 exfoliation for the moderate exfoliation energy. The synthesis and crystal structure of
13 bulk InP_3 was first reported by Kinomura, and the bulk InP_3 is stability at ambient
14 conditions [22]. With a suitable band gap (1.14 eV), high electron mobility
15 ($1919 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), high-mobility transport anisotropy (armchair and zigzag
16 direction) and great optical performance, it suggests that the 2D InP_3 is a
17 promising candidate material for future applications in electronics and
18 optoelectronics [21]. Recently, Liu and co-workers [23] theoretically predicted
19 monolayer InP_3 as a reversible anode material for ultrafast charging lithium-
20 and sodium-ion batteries.

21 From the perspective of the sensing mechanism, the semiconductor type gas
22 sensor works based on the change of the conductivity of the sensitive material

1 caused by adsorption of gas molecules onto its surface [3, 24]. In order to
2 increase the detection limit of this type gas sensor, an effective method is to
3 enhance the interaction between gas molecules and sensitive materials, and the
4 resulting stronger adsorption and more charge transfer will lead to greater
5 changes in conductivity, which in turn will increase sensitivity [25]. It was also
6 found that the gas-sorbent interaction and gas-sensing characteristic depend largely on
7 the surface structure and properties of the sensitive materials. The structure of InP_3
8 is closely related to that of arsenic, replacing systematically every fourth atom
9 in the arsenic layer by an indium (In) atom and the rest by phosphorus (P) atom.
10 Their monolayer structures are similar, except that the surface of arsenene [26]
11 is composed only of As atoms, while the compositions of InP_3 monolayer are P
12 and In atoms. To the best of our knowledge, surface component of most 2D
13 materials is single element. Take TMDs and MXenes as examples, their
14 monolayers are composed of separate metal and non-metal atomic layers. While
15 in InP_3 , every layer is consisted of both metal atoms (In) and non-metal atoms
16 (P). It can be speculated that the unique structure of InP_3 monolayer may cause
17 rather different gas sensing behaviour. Therefore, it is of necessity to theoretically
18 study the interaction between the surface of this sensitive material and gas molecules.
19 In this regard, calculation based on the first principle can provide reliable information
20 such as adsorption energy and electronic properties of the adsorption system. In
21 addition, the calculation of adsorption of NO_x on ZnO [6, 27], and SO_2 on graphene
22 have been completed, which make sure theoretical calculation is a powerful tool that

1 can help us to choose the sensitive material and experiment routine. Meanwhile, the
2 modification of surface structure by doping and strain has been proposed and
3 demonstrated as an efficient way to modify the electronic, magnetic, chemical,
4 and sensing properties of materials [28, 29].

5 In this work, the adsorptions of HCHO and its various possible organic
6 interfering gases (including C₂H₆, C₂H₄, C₂H₂, C₆H₆ and C₂H₅OH) on InP₃
7 monolayer were calculated based on density functional theory (DFT)
8 simulations. To explore the sensitivity and selectivity of gas sensor based on
9 InP₃, The properties of the gas/InP₃ adsorption systems including adsorption
10 energy (E_a), adsorption distance (d), charge transfer (ΔQ), total and partial
11 densities of states (DOS and PDOS) and recovery time were calculated. The
12 possible sensing mechanism was also explored by comparing the adsorption of
13 HCHO on three types of 2D materials (graphene, single-layered MoS₂ and InP₃
14 monolayer) with different structure features. The study on the adsorption site of
15 HCHO and the steric effect of the site on sensitive materials were conducted,
16 indicating that structure of sensing material plays an important role in the
17 detection of HCHO. Then, the performance optimization of HCHO sensor was
18 also performed by applying strain on InP₃ monolayer, which shows that
19 strained InP₃ monolayer is more sensitive and selective to HCHO.

20 **2 Computational details**

21 The first-principle calculations of structural optimization and electronic
22 properties are performed on the basis of DFT as implemented in the DMol³

1 package. The exchange correlation interaction is treated through a general
2 gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE)
3 function [30]. The dispersion corrected DFT-D proposed by Grimme has been
4 employed in order to investigate the interactions between the organic gas
5 molecules and monolayer material. The convergence criteria of self-consistent
6 field energy, the MAX force and the maximum displacement are 1.0×10^{-5} eV,
7 0.002 eV/Å, and 5.0×10^{-3} Å, respectively. The Brillouin zone integration is
8 done by setting a $12 \times 12 \times 1$ Monkhorst-Pack k -point grid for a $2 \times 2 \times 1$ InP₃
9 supercell for both geometry optimization and electronic properties calculations,
10 while the structure of graphene is obtained on the foundation of a $4 \times 4 \times 1$
11 supercell. The thickness of a vacuum region in the Z direction is kept as 20 Å to
12 avoid the effect of interaction deriving from the adjacent layer.

13 The adsorption energy (E_a) is defined as follows:

$$14 \quad E_a = E(\text{sub+gas}) - E(\text{sub}) - E(\text{gas}) \quad (1)$$

15 where $E(\text{sub+gas})$, $E(\text{sub})$ and $E(\text{gas})$ are the total energy of gas/substrate
16 adsorption system, isolated substrate and the separated organic gas molecules,
17 respectively.

18 The adsorption distance (d) is defined as the vertical distance between the
19 lowest atom of the gas molecule and the top atom of InP₃ monolayer. The
20 charge transfer (ΔQ) of the gas molecules adsorbed on InP₃ monolayer can be
21 studied using Mulliken population analysis [31]. A positive value of ΔQ means
22 the charges transfer from gas to the surface of substrate.

1 The charge density difference (CDD) is calculated by the following formula:

$$2 \quad \Delta\rho = \rho(\text{sub+gas}) - \rho(\text{sub}) - \rho(\text{gas}) \quad (2)$$

3 where $\rho(\text{sub+gas})$, $\rho(\text{sub})$ and $\rho(\text{gas})$ are the charge densities of the gases
4 adsorption system, substrate, and separated organic gas molecule, respectively.

5 The electron localization function (ELF) is carried out using CASTEP code.
6 The energy cutoff is set as 500.0 eV and the ultrasoft pseudopotentials are
7 adopted.

8 **3 Results and discussion**

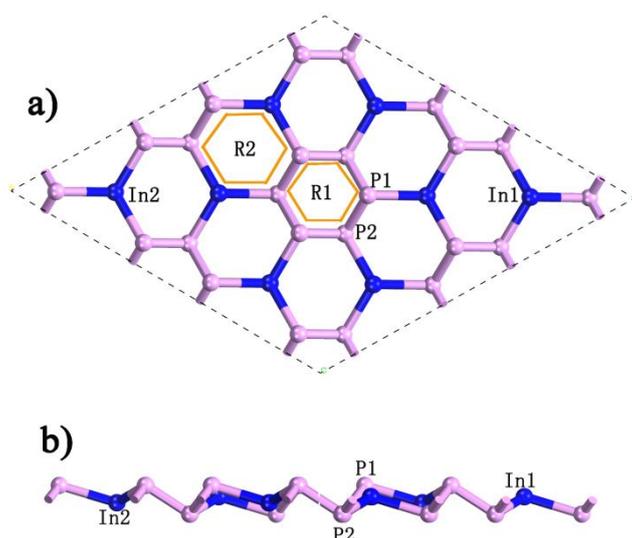
9 We first tested the accuracy of our computational method by calculating the
10 lattice constants of unit cell of InP_3 monolayer and graphene. The values are
11 7.535 Å and 2.466 Å, respectively, which are in agreement with the previously
12 reported results [21, 32, 33].

13 **3.1 The adsorption of organic gases on InP_3 monolayer**

14 To explore possible sensitivity and selectivity of InP_3 monolayer to HCHO,
15 C_2H_6 , C_2H_4 , C_2H_2 , C_6H_6 , $\text{C}_2\text{H}_5\text{OH}$ and HCHO are chosen as adsorbates. The
16 adsorption sites and configurations are determined by analysing the structure
17 feature of InP_3 monolayer.

18 InP_3 monolayer exist two kinds of six-membered rings, one is formed by six
19 P atoms (R1) and the other includes four P atoms and two para-position In
20 atoms (R2). As shown in Fig. 1(a), each In atom is bonded with three P atoms
21 from three separate R1s and each P atom is bonded with one In atom. There are
22 also two kinds of In and P atoms due to both two rings are exhibit chair

1 conformation, which are named as In1, In2, P1 and P2, respectively.
2 Considering the complexity of InP₃ monolayer structure, a number of
3 adsorption sites including P1 atom, P2 atom, In1 atom, In2 atom, the centre of
4 R1 and the centre of R2 are taken into account with a reason that gas molecules
5 with different structures tend to be adsorbed in different sites and
6 configurations. To this end, the single gas molecule of C₂H₆, C₂H₄, C₂H₂, C₆H₆,
7 C₂H₅OH and HCHO was placed at a distance of 3Å above the adsorption sites
8 mentioned above to find the one with lowest adsorption energy. At these
9 particular positions, several molecular orientations were also considered. Take
10 HCHO molecule as an example, three orientations of the HCHO molecule were
11 investigated, with the H atom, O atom and C atom pointing to the surface of
12 InP₃, respectively.



13
14 Fig. 1 Top (a) and side (b) view of the optimized structural (supercell) model of InP₃ monolayer

15 The interaction between gas and InP₃ monolayer can be described regarding
16 their E_a . Based on Eq. (1), the more negative the value of E_a is, the stronger

1 adsorption of gas molecules on InP₃ would be. The most energetically
 2 favourable adsorption configurations for all gases mentioned above are selected
 3 for further studies, and Fig. S1 presents the lowest energy configurations. And
 4 the E_a aforementioned of gas molecules onto InP₃ monolayer, the adsorption
 5 distances, and the charge transfers are listed in Table 1.

6 Table 1 Adsorption energy (E_a), adsorption distance (d), charge transfer (ΔQ) and the related covalent
 7 radii (r) between InP₃ monolayer and organic gas molecules (C₂H₆, C₂H₂, C₂H₄, C₆H₆, C₂H₅OH, and
 8 HCHO)

Gas molecule	E_a (eV)	ΔQ (e)	d (Å)	r (Å)
C ₂ H ₆	-0.3118	-0.07	2.819	2.44(H-In)
C ₂ H ₄	-0.7488	0.063	2.672	2.52(C-In)
C ₂ H ₂	-0.5867	0.088	2.718	2.52(C-In)
C ₆ H ₆	-0.9290	0.004	2.752	2.52(C-In)
C ₂ H ₅ OH	-1.1186	0.175	2.322	2.32(O-In)
HCHO	-1.2974	-0.368	1.933	2.12(C-P)

9

10 For C₂H₆ molecule, the steadiest configuration is presented in Fig. S1(a),
 11 where the C-C single band seemingly parallel to the monolayer and the
 12 adsorption distance is 2.819 Å. In the case of C₂H₄ adsorption, the most
 13 favourable adsorption configuration based on the lowest adsorption energy is
 14 exhibited in Fig. S1(b), where the plane of C₂H₄ molecule is aligned parallel to
 15 InP₃ monolayer surface with the C-C double band directly above the In1 atom.
 16 The configuration of C₂H₂ adsorption is similar to C₂H₄, Fig. S1(c) shows the
 17 C-C triple band directly above the In1 atom and the adsorption distance is 2.718
 18 Å, larger than that of C₂H₄ (2.672 Å). All atoms of C₆H₆ are in a plane that is
 19 not parallel to InP₃ monolayer and forms a specific angle, as shown in Fig.

1 S1(d). Fig. S1(e) shows the adsorption configuration of C_2H_5OH molecule,
2 where O atom closes to In1 atom. These adsorption systems hardly caused
3 deformation of the InP_3 monolayer. While for HCHO, the structures of both
4 HCHO molecular and monolayer have changed. HCHO prefer to locate parallel
5 to the monolayer with O atom upon In1 atom and C atom upon P1 atom, and
6 the distance between In1 and P1 ($d1 = 3.392 \text{ \AA}$) is smaller than others (from $d2$
7 to $d6$), as shown in Fig. S1(f).

8 According to the calculation results, adsorption strength changes in the
9 following order: $HCHO > C_2H_5OH > C_6H_6 > C_2H_4 > C_2H_2 > C_2H_6$. The E_a
10 (-1.2974 eV) of HCHO is the most negative one, implying that InP_3 monolayer
11 exhibits excellent HCHO gas sensing performance. Besides, the charge transfer
12 of HCHO (-0.368 e) is the largest of all studied gases. This means that when
13 HCHO adsorbed on InP_3 monolayer, it may cause large changes in the electrical
14 signal, resulting in a lower detection limitation. The HCHO molecule behaves
15 as electron acceptors for the charges transfer from the substrate to it.

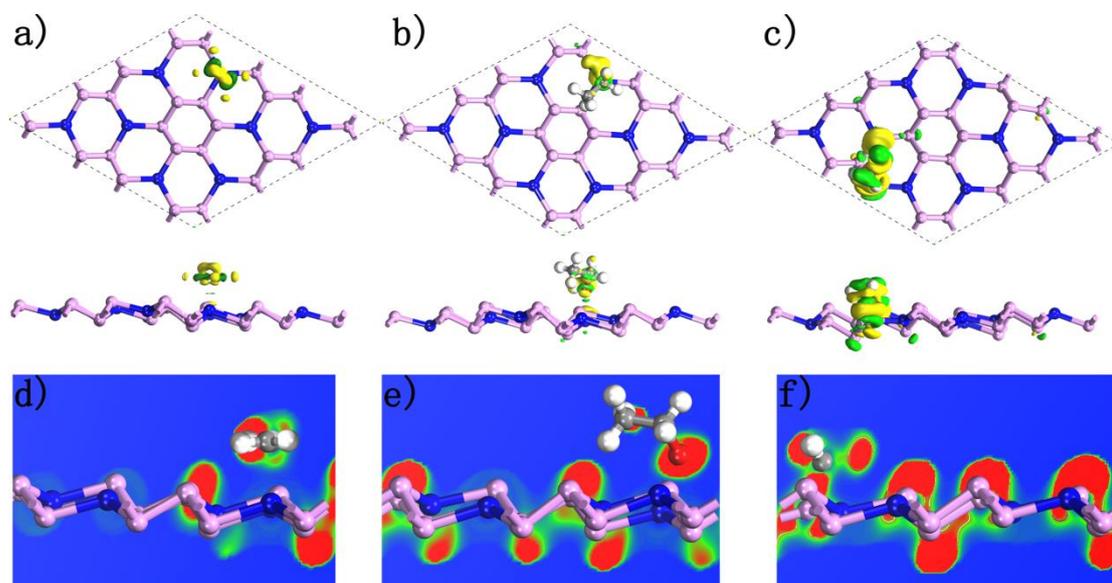
16 For C_2H_5OH/InP_3 adsorption system, the absolute value of E_a (1.1186 eV) and
17 ΔQ (0.175 e) are obtained, which are smaller than that of HCHO/ InP_3 system,
18 but are still larger than the values of other four hydrocarbons gases. The
19 distances are 1.933 \AA and 2.322 \AA for HCHO/ InP_3 and C_2H_5OH/InP_3 ,
20 respectively. They are less than the sum of covalent radii (2.12 \AA for In-O and
21 2.32 \AA for In-C), indicating that HCHO may be chemisorbed on InP_3
22 monolayer. The difference between HCHO and C_2H_5OH when adsorbed on

1 InP₃ monolayer may be due to the steric effect of the hydrogen atoms on the
2 hydroxyl groups in C₂H₅OH, preventing C₂H₅OH and InP₃ monolayer from
3 getting closer. Therefore, the interaction between HCHO and the substrate is
4 stronger than C₂H₅OH.

5 Compared with these two oxygen-containing molecules, the absolute value
6 of E_a and ΔQ of other four hydrocarbons molecules are much lower. For
7 C₆H₆/InP₃ adsorption system, the E_a is -0.9290 with a ΔQ of 0.004 e, which
8 suggests that C₆H₆ adsorption strength is weak. When C₂H₄ adsorbed on InP₃
9 monolayer, there is a relatively large adsorption strength (-0.7488 eV) and
10 charge transfer (0.063 e) among hydrocarbon molecules. And the adsorption
11 distance is 2.672 Å, which is greater than the sum of their covalent radii (2.52
12 Å). This may means that all these hydrocarbon molecules are physically
13 adsorbed on InP₃ monolayer.

14 In this part we focus primarily on exploring the deeper interaction mechanism
15 between adsorbates and InP₃ monolayer. The charge density difference (CDD)
16 of C₂H₄/InP₃, C₂H₅OH/InP₃ and HCHO/InP₃ adsorption systems were
17 calculated and presented in Fig. 2(a)(b)(c), the charge accumulation is
18 represented by green colour, whereas yellow represents the charge depletion
19 region. As shown in Fig. 2(a), there is rarely charge density redistribution
20 between C₂H₄ and InP₃ monolayer, implying that their interaction is weak and
21 no chemical bond is formed. While for oxygen-containing gases, the charge
22 density redistribution is more obvious, and the most apparent is HCHO

1 adsorption. Fig. 2(b) shows that the charge density redistribution of
 2 C_2H_5OH/InP_3 adsorption system. In Fig. 2(c), the charge density redistributes
 3 of the $HCHO/InP_3$ system is mainly induced by the strong interaction between
 4 O atom of HCHO molecule and In1 atom of InP_3 monolayer. There is a
 5 significant depletion of charge density between O atom and In atom, suggesting
 6 the covalent bond may partly formed between HCHO and InP_3 monolayer.



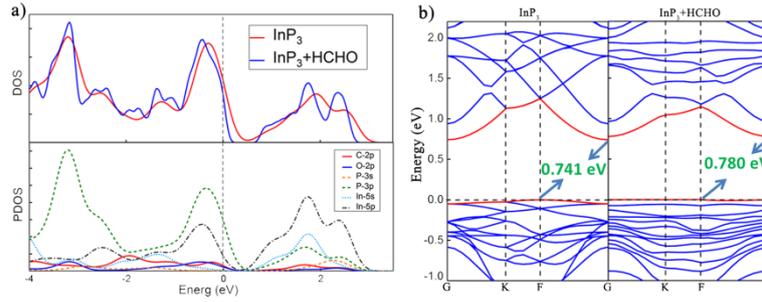
7
 8 Fig.2 The CDD of (a) C_2H_4 , (b) C_2H_5OH and (c) HCHO on InP_3 monolayer. The isosurface value is $0.02 e/\text{\AA}^3$. The
 9 green region shows the charge accumulation, whereas the yellow region represents the charge depletion. (d)(e)(f)
 10 present the corresponding ELF plots.

11 Besides, the corresponding ELF charts of the above three systems are
 12 presented in Fig. 2(d)(e)(f). As shown in Fig. 2(d), the electron localization of
 13 InP_3 monolayer and C_2H_4 is separated, further demonstrating that there is no
 14 chemical bond between C_2H_4 gas and the monolayer. The interaction between
 15 C_2H_4 and InP_3 is composed by weak van der Waals force, and it is quite sure
 16 that C_2H_4 is physical adsorbed on InP_3 . As shown in Fig. 2(e), the ELF of
 17 C_2H_5OH/InP_3 system is similar to C_2H_4/InP_3 system, and the electron
 18 localization does not overlap, which means that there may also no chemical

1 bond formed between C_2H_5OH and InP_3 monolayer. While for HCHO, the
2 overlap of electron localization means that adsorption of HCHO is stronger
3 than other gases and may chemisorption, further illustrating that the material is
4 more sensitive to HCHO, Fig. 2(f).

5 To further explore the sensitivity of InP_3 monolayer towards HCHO gas molecule,
6 DOS, PDOS and band structure were calculated and described in Fig. 3. After
7 adsorption of HCHO on InP_3 , significant change of DOS near Fermi level can be seen
8 from Fig. 3(a). The adsorption of HCHO leads to noticeable perturbation to the DOS
9 of InP_3 substrate, including the movement of peaks and the generation of new peaks.
10 Simultaneously, there are orbital hybridizations according to the states of O-2p, P-3p
11 and In-5p orbitals between -2 and 0 eV; and other two orbital hybridizations between
12 0 and 3.5 eV, not only including C-2p, P-3p, In-5s and In-5p but also O-2p, P-3s, P-3p
13 and In-5p. These make clear that the sensitivity of InP_3 to HCHO. From the changes
14 of band structure, Fig. 3(b), it is noted that the adsorption of HCHO onto InP_3 causes
15 the conduction bands to move slightly towards higher energy level, indicating that the
16 band gap of HCHO/ InP_3 system slightly increased from 0.741 eV to 0.780 eV and the
17 conductivity has a slight decrease compare with that of isolated InP_3 .

18



1

2 Fig. 3.(a) DOS (up) of InP_3 with and without HCHO, and PDOS (down) of HCHO/ InP_3 system. (b)
 3 Band structures of pristine InP_3 (left) and HCHO adsorbed on pristine InP_3 (right).

4 The analysis of E_a , d , ΔQ , CDD and ELF indicate that the adsorptions of
 5 oxygen-containing gases onto InP_3 monolayer are much more effective than
 6 that of oxygen-free gases, which is consistent with the previous reported
 7 experiment results [5, 25, 34, 35], that is, the sensitive materials of HCHO
 8 sensor are sensitive to oxygen-containing gases than oxygen-free gases. Then
 9 the deeper understanding of the interaction mechanism between adsorbates and
 10 InP_3 monolayer is essential, which will helpful in further enhancing the
 11 performance of HCHO sensor.

12 3.2 Adsorption of HCHO on different 2D materials

13 In this section, the other two 2D materials with different structures, namely
 14 graphene and single-layered MoS_2 , were selected as the substrate for adsorbing
 15 HCHO. The adsorptions of a single HCHO molecular on the top of these layer
 16 materials were compared with each other and the configurations with the largest
 17 absolute value of adsorption energy (E_a) were presented in Fig. 4, the values of
 18 E_a , d and ΔQ were also listed in Table 2. In order to find out the structural
 19 feature causing the strong interaction between HCHO and InP_3 monolayer, an

1 in-depth comparison and analysis of the structural differences and
2 corresponding calculation results of these three materials was conducted.

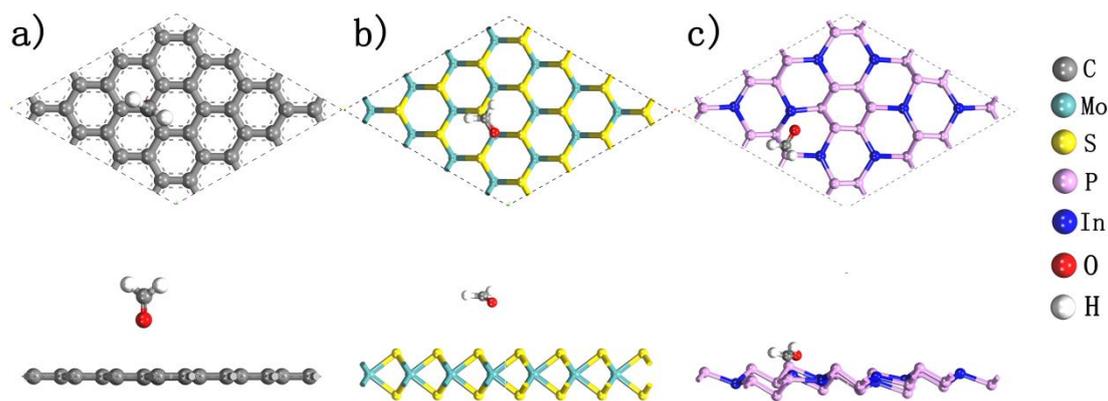
3 Table 2 Adsorption energy (E_a), adsorption distance (d), and charge transfer (ΔQ) between HCHO and 2D
4 materials (InP₃ monolayer, graphene and single-layered MoS₂).

5

substance	E_a (eV)	d (Å)	ΔQ (e)
InP ₃	-1.2974	1.933	-0.368
graphene	-0.0716	2.993	0.016
MoS ₂	-0.03	3.74	0.01

6 In Fig. 4(a), HCHO molecule is perpendicular to the surface of graphene. Fig.
7 4(b) shows HCHO/MoS₂ system, the HCHO molecular is seemingly parallel to
8 the surface of MoS₂ monolayer. In HCHO/InP₃ system, the HCHO is also
9 seemingly parallel to the surface of InP₃ monolayer with O atom upon In1 atom
10 and C atom upon P1 atom, as shown in Fig. 4(c). The structure of HCHO has
11 also changed, that is, the four atoms of a simple HCHO molecule without
12 adsorption are in the same plane, while HCHO of the adsorption system is not a
13 planar molecule. The largest absolute value of E_a and ΔQ for HCHO on InP₃
14 are 1.2974 eV and -0.368 e, respectively, which are larger than the
15 corresponding values of HCHO on graphene (0.0716 eV and 0.016 e) and MoS₂
16 (0.03 eV and 0.01 e) [36].

17



1

2

Fig. 4 The structure of HCHO adsorbed onto (a) graphene, (b) single-layered MoS₂ and (c) InP₃ monolayer.

3

3.2.1 The influence of electronegativity

4

The weak adsorption of HCHO onto graphene and single-layered MoS₂ may

5

result from the large electronegativity of C (2.55) and S (2.58). As shown in

6

previous reports, HCHO molecule often behaved as an electron acceptor and

7

thus the strong interaction between HCHO and the substrates often involve

8

significant electron transfer from the substrates to the molecule and the charge

9

transfer is negative [12-14, 36]. As a result, the large electronegativity of S

10

atom may make it difficult for HCHO to grab electrons from MoS₂ and thus

11

prevent the strong interaction between them. The adsorption of HCHO onto

12

graphene is similar. Compared with C and S atom, the electronegativity of In

13

atom (1.78) is smaller, which may be a reason why adsorption of HCHO onto

14

InP₃ monolayer is stronger than that of graphene and single-layered MoS₂.

15

3.2.2 The influence of structure and polar bond

16

On the other side, the difference of interaction between HCHO and these 2D

17

materials is related to the difference in materials' structures, which can be seen

18

from Fig. 4. Graphene is composed of a hexagonal-close-packed carbon

19

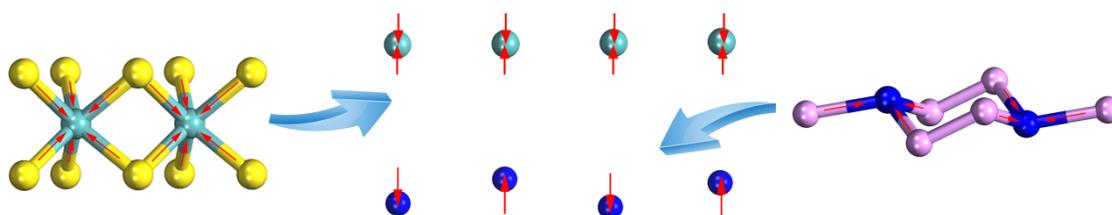
network, in which each atom covalently bonds to three neighbouring ones

1 through σ -bond [37], and a theoretically plane with uniformly distributed
2 charge is formed, Fig. 4(a). The monolayer structure of MoS_2 is shown in Fig.
3 4(b), and it is consist of three atomic layers, one Mo layer and two S layers [38,
4 39]. The Mo layer is electropositive and the S layers are electronegative, then
5 the Mo layer is sandwiched between two S layers and seems like shielded by
6 them. Besides, InP_3 monolayer is a puckered honeycomb structure, the surface
7 of which is composed of In and P atoms, Fig. 4(c).

8 Since HCHO is a polar molecule and the O atom has a large electronegativity,
9 when this molecule was placed on graphene that is a nonpolar substance, the
10 interaction between them may be only dispersion force and induction force.
11 These forces are both very weak. MoS_2 is also a non-polar molecule, however,
12 its chemical bonds are polar and there are dipole moments in the opposite
13 direction across the entire plane, and the orientation of all dipoles in MoS_2 is
14 from S atom layer to Mo atom layer, as shown in Fig. 5. The small angle of
15 S-Mo-S (86.803°) makes the electronegative S atoms prevent the
16 electronegative O atoms from coming close to Mo atoms, and MoS_2 is difficult
17 to form a strong orientation force with HCHO. Therefore, the adsorption
18 strength of HCHO on graphene and MoS_2 is weak. Unlike graphene, InP_3
19 monolayer has polar bonds, which are also different from MoS_2 because its
20 electropositive atoms (In) are not protected by electronegative atoms (P).
21 Strong dipole-dipole force can be formed between the dipole moment existed in
22 InP_3 and HCHO, which may greatly enhance their interaction. Compared with

1 MoS₂, the structure of InP₃ monolayer is close to a plane, which makes it easier
2 for HCHO to adsorb onto its favourite position, that is, O atom on the top of
3 electropositive atom and C atom on the top of electronegative atom. The
4 enhanced dipole-dipole force results in a higher E_a value.

5 The above analyses show that the interaction between HCHO and these 2D
6 materials may be adjusted by applying strain to the material. Take MoS₂ as an
7 example, the strain may increase the angle of S-Mo-S and thus reduce the
8 shielding effect of S atoms to Mo atoms. Kou et al. reported the strain
9 engineering of chemical adsorption on MoS₂ monolayer [40]. It was found that
10 the charge transfer in the strain-free layer is limited between the gas molecule
11 and the most adjacent S atom, and by contrast some electrons transfer to Mo
12 atoms and become slightly delocalized after applying strain on the monolayer.
13 As a result, the gas molecules are getting closer to the MoS₂ monolayer, which
14 increases the absolute value of E_a .



15
16 Fig. 5 The partial structures of MoS₂ (left) and InP₃ (right) and the red arrow present the orientations of the dipole
17 of chemical bonds, between them are the metal atoms extracted from each structure and present the orientations of
18 the dipole moment.

19 **3.3 Enhancement of HCHO sensing performance by strain engineering**

20 To confirm that the adsorption strength can be tuned by the application of
21 strain on monolayer, the adsorption of HCHO onto the strained InP₃ monolayer
22 was calculated, in which four typical strained states (2%, 4%, 6% and 8%)

1 along a -direction were implemented. The structure of InP₃ monolayer affected
2 by strain can be seen in Fig. S2.

3 Fig. 6 shows the changes in a few parameters caused by strain, including the
4 distance between In2 atom and O atom ($d_{\text{In2-O}}$), adsorption energy and the rate
5 of change of distance between In1 atom and P1 atom (R_d). The R_d is defined as:

$$6 \quad R_d = |d'_{\text{In1-P1}} - d_{\text{In1-P1}}| / (d_{\text{In1-P1}}) \quad (3)$$

7 where $d_{\text{In1-P1}}$ and $d'_{\text{In1-P1}}$ are the distance between In1 atom and P1 atom of InP₃
8 monolayer before and after adsorption of HCHO, respectively.

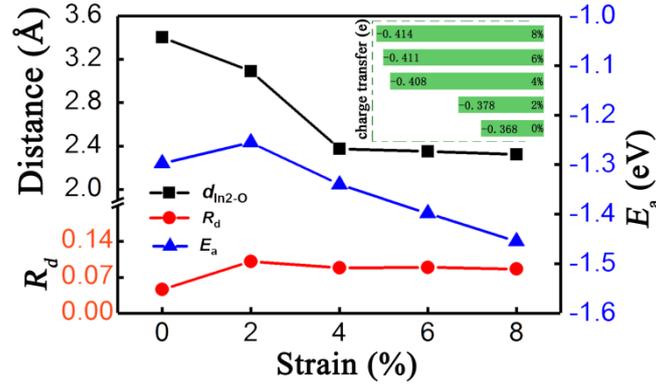
9 As shown in Fig. 6, E_a (blue line) of HCHO/strained-InP₃ system briefly
10 increase as the strain rises from 0 to 2%, then decrease with the rising strain
11 from 2% to 8%. After applying the strained state of 4% to InP₃ monolayer, the
12 absolute value of E_a is larger than pristine InP₃, and this value progressively
13 increase as the strain rises. It also shows charge transfer (the upper right corner
14 of Fig. 6) systematically enhanced with increasing strain, going from -0.368 e
15 at 0% strain to -0.408 e at 4% strain according to Mulliken charge analysis. It is
16 clear that adsorption strength of HCHO on InP₃ can be enhanced by the
17 application of strain, thus the performance of HCHO sensor based on strained
18 InP₃ can also be promoted.

19 In Fig. 6, the variation of R_d (red line) with strain is almost the same as E_a ,
20 except that the value of R_d is always greater than that of the pristine InP₃. A
21 continuous reduction of the value of $d_{\text{In2-O}}$ (black line) is caused by decrease of
22 the shielding effect of P1 atom on In2 atom with increasing strain. Therefore, it

1 is easier for O atom to get closer to In2 and form a stronger interaction. The
2 smaller the distance is, the stronger the interaction between these two atoms is.
3 It suggests that increasing interactions will lead to a more negative E_a value,
4 which is why E_a will decline as the strain increases from 2% to 8%.

5 The following explains why 2% strain is the turning point of adsorption
6 energy. As mentioned earlier, the E_a of HCHO/InP₃ system is related to the
7 distance of In1-P1. This is because the most favourable adsorption positions of
8 the HCHO molecule adsorbed on InP₃ monolayer are O atom onto In1 atom
9 and C atom onto P1 atom, respectively. As shown in Fig. S2, it was found that
10 the adsorption process has caused obvious geometric changes on the monolayer.
11 After InP₃ monolayer was strained, the In1-P1 distance increased, which means
12 that the R2 ring needs more energy to distort itself to satisfy the adsorption of
13 HCHO molecule on its favourable position. As a result, the adsorption strength
14 decreases, in other words, the value of E_a increases. Therefore, E_a of HCHO
15 adsorption increases first and then decreases with increasing strain.

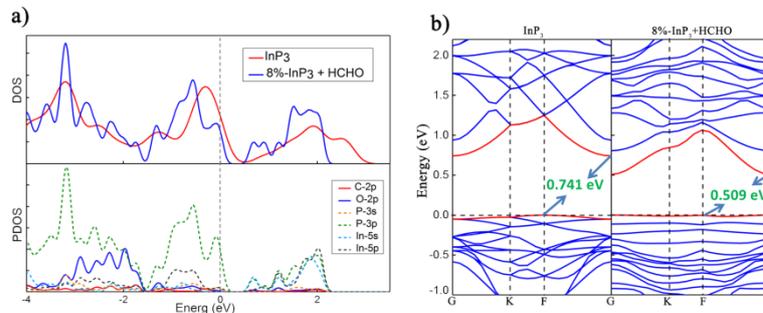
16 When it comes to C₂H₅OH, the variation of E_a completely differs from
17 HCHO, as shown in Table. S1. The absolute value of E_a is 1.1186 eV when
18 C₂H₅OH adsorbed on pristine InP₃ monolayer. It decreases from 1.0589 eV to
19 0.9791 eV as the strain increases from 2% to 8%. The charge transfer also
20 decrease with increasing strain, which is opposite of HCHO. Therefore, to a
21 certain extent, strain can improve the selectivity of HCHO sensor based on InP₃
22 monolayer.



1

2 Fig. 6 The change curves of E_a (blue), R_d (red) and $d_{\text{In2-O}}$ (black) accompany with strain in HCHO/strained-InP₃
 3 systems. The insert presents the charge transfer of the HCHO/strained-InP₃ systems.

4 The DOS, PDOS and the band structure of HCHO onto 8%-strained InP₃
 5 were also calculated and described in Fig. 7. As shown in the Fig. 7(a), the new
 6 peak appearing near the Fermi level (localized at -0.0797 eV) in DOS and the
 7 strong hybridization of orbitals in the PDOS reveal that the strong interaction
 8 between HCHO molecule and 8%-strained InP₃, which is consistent with
 9 previous result that the strain can increase adsorption strength between HCHO
 10 and InP₃. As for the band structure, when HCHO adsorbed onto the 8%-strained
 11 InP₃, band gap [see Fig. 7(b)] decreased from 0.741 eV to 0.509 eV, indicating
 12 the conductivity has a significant increase compared with that of pristine InP₃,
 13 which can be explained by the appearance of the new peak near the Fermi level
 14 in Fig 7(a).



15

16 Fig. 7. (a). The total (up) and partial (down) densities of states. (b) Band structure for HCHO adsorbed on
 17 8%-strained InP₃ monolayer based on the most stable configuration

1 3.4 recovery time

2 Since InP₃ is a potential sensitive material, it is worthy to talking about the
3 recovery time which is one of the important factors for gas sensor. According to
4 the transition state theory [41], the recovery time τ can be calculated by the
5 formula (4):

$$6 \quad \tau = \omega^{-1} \exp(E^*/K_B T) \quad (4)$$

7 where T is the temperature, K_B is the Boltzmann' Constant, E^* is the desorption
8 energy barrier and ω is the attempt frequency. The transition state of desorption
9 process of HCHO from pristine InP₃ and 8% strained InP₃ can be found by
10 calculating the minimum-energy path (MEP) [42] and then calculated the value
11 of E^* . The initial state was the configuration with the HCHO adsorbed on InP₃,
12 and the final state was set to be the configuration that HCHO parallel with the
13 InP₃ at a distance of 3Å above the favourite adsorption sites. As a result, the
14 calculated desorption energy barrier for both of these two systems are equal to
15 their adsorption energy, which are 1.2974 eV and 1.4547 eV, respectively. The
16 higher desorption barrier suggests a longer recovery time of HCHO on
17 substrate at the same temperature. Suppose ω is 10^{13} s^{-1} [43, 44], then pristine
18 InP₃ will has a recovery time of about 1 s at the temperature of 500 K and 1700
19 s at 400 K, and the recovery time for strained-InP₃ is 45 s at the temperature of
20 500 K. The results are similar with several recently reported HCHO sensors
21 [45-47].

22 4 Conclusion

1 In conclusion, the adsorption of a few organic gases including C_2H_6 , C_2H_4 ,
2 C_2H_2 , C_6H_6 , C_2H_5OH and HCHO on InP_3 monolayer are calculated, and the
3 properties of the gas/ InP_3 systems including adsorption energy (E_a), adsorption
4 distance (d), charge transfer (ΔQ), DOS, band structure and recovery time are
5 obtained. With E_a of -1.2974 eV and ΔQ of -0.368 e, InP_3 monolayer has high
6 sensitivity and selectivity to HCHO. The most favourable adsorption geometry
7 configuration for HCHO adsorbed on InP_3 monolayer, graphene and MoS_2
8 were also compared, and the results prove that the E_a of HCHO adsorbed on
9 InP_3 monolayer is much larger than that of graphene and MoS_2 . The
10 phenomenon is explained by the polarity and structural feature of these 2D
11 materials. And to further explain the importance of the material structure, the
12 effects of strain on the HCHO/ InP_3 and C_2H_5OH/InP_3 adsorption systems were
13 also calculated. As the strain increases from 0% to 8%, the absolute value of E_a
14 increases from 1.2974 eV to 1.4547 eV, and the charge transfer vary from
15 -0.368 e to -0.414 e, indicating an enhancement of the interaction between
16 HCHO and InP_3 monolayer. While for C_2H_5OH , adsorption strength and charge
17 transfer both decreases. These results show that strained InP_3 monolayer is
18 more sensitive and selective to HCHO than the pristine. The theoretical
19 calculations suggest that InP_3 monolayer could be an extremely promising
20 sensor material for the detection of HCHO. More importantly, application of
21 strain on the sensitive material is proven to be an efficient way to improve the
22 performance of HCHO sensor, which may shed a light on the related research.

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