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Superior and tunable gas sensing properties of Janus PtSSe monolayer

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Abstract

Inspired by superior gas sensing properties of $PtSe_2$ monolayer and tunable gas sensing properties of Janus MoSSe monolayer, we study the gas sensing properties of the Janus PtSSe monolayer for CO, CO_2, H_2O, NH_3, NO and NO_2 gas molecules using first-principles density functional calculations. We calculate adsorption height and adsorption energies of the gas molecules to assess the adsorption strength of the gas molecules. Then the charge transfer from PtSSe to gas molecules is evaluated. We also investigate the effects of strain and external electric field on the gas sensing properties of Janus PtSSe monolayer. We finally reveal the origin of the superior gas sensing properties from projected density of states analysis. Our results suggest that the Janus PtSSe monolayer is a promising gas sensor with superior and tunable sensing properties.

1. Introduction

Sensing of gas molecules is a vital task in pollution monitoring and medical applications [1]. Due to a large portion of atoms can be exposed to and having charge transfer with gas molecules, two-dimensional (2D) materials have attracted much attention for gas sensing. Graphene as the first member of the 2D materials, however, fails to serve this purpose with only limited sensing ability due to its metallic nature [2, 3]. Transition metal dichalcogenides(TMDs), such as MoS_2, are semiconducting 2D materials with tunable electronic properties upon gas molecule adsorption therefore performing well as gas sensors [4–14]. Recently, semiconducting monolayer $1T-PtSe_2$ has been experimentally achieved with enhanced carrier mobility [15, 16]. It is then proposed that $1T-PtSe_2$ has superior sensing properties [17].

2D Janus materials with planar asymmetry have drawn much attention due to their unique physical properties and potential applications [18–31]. The Janus TMDs have different atomic species at each side of the metal layer, which induce a large electric dipole across the plane. Due to the electric dipole, an intrinsic built-in electric field is formed across the plane. Up to date, one of the Janus TMDs, MoSSe, has been experimentally synthesized by chemical vapor deposition (CVD) [18, 32]. The Janus MoSSe monolayer is proposed as a superior and strain-sensitive gas sensor owing to its built-in electric field [33]. Janus PtSSe monolayer as an emerging Janus TMDs has been suggested also as charge separating materials and contacts for graphene [29–31]. Regarding superior gas sensing properties of $PtSe_2$ and MoSSe, it is desirable to explore the gas sensing properties of the Janus PtSSe monolayer, as studied before like MoSSe [33].

In this work, we investigate the gas sensing properties of the Janus PtSSe monolayer for typical gas molecules CO, CO_2, H_2O, NH_3, NO and NO_2 by density functional calculations. Firstly, the adsorption strength is assessed from adsorption height and adsorption energies of the gas molecules on S-layer and Se-layer of the Janus PtSSe monolayer. Charge transfer from substrate to the gas molecules is evaluated after adsorption. Effects of strain and external electric field modulation of the adsorption properties are systematically studied. Finally, the projected density of states (DOS) were analysized to reveal the origin of the superior gas sensing properties. Our

results suggest that the Janus PtSSe monolayer is a promising gas sensor with superior and tunable sensing properties better than MoSSe.

2. Methodology

Density functional theory (DFT) calculations as implemented in the Vienna *Ab initio* Simulation Package (VASP) [34, 35] were carried out to relax the geometry structures of the molecules adsorption on the Janus PtSSe monolayer and investigate the adsorption properties. A kinetic energy cut-off of 500 eV was used for plane-wave expansion and a gamma-centered Monkhorst–Pack [36] Brillouin zone k-point sampling grid of $5 \times 5 \times 1$ was adopted to ensure the accuracy. For atomic geometry optimization, the atomic force tolerance was set to 0.01 eV/Å for better accuracy. For the exchange-correlation functional, the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof functional (PBE) [37] was utilized. To take into account the weak van der Waals (vdW) interactions in the calculations, the DFT-D3 method under the Grimme scheme [38, 39] was included. Spin-polarized calculations were carried out for the adsorption of the NO and NO_2 gas molecules. Our calculated lattice parameter of the Janus PtSSe monolayer is $a = 3.66$ Å, which is in good agreement with previous calculated results [31]. Based on this lattice parameter, a $4 \times 4 \times 1$ supercell of Janus PtSSe monolyer with one gas molecule adsorbed was built as the computational model. A vacuum layer of 18 Å was inserted between the monolayers to eliminate the interactions from periodic slab images. Charge transfer between the Janus PtSSe monolayer and the adsorbed molecules was evaluated by Bader analysis [40].

3. Results and discussion

The Janus PtSSe monolayer consists of a Pt atomic layer sandwiched between a S atomic layer and a Se atomic layer. A top view shows a hexagonal structure with Pt and S atoms located at nearby corners and an additional Se atom located in the center of each hexagon. To identify the most energetically favorable adsorption configuration for each gas molecule, several possible adsorption sites were considered, such as the top site above the center of the hexagon, the top above the Pt (S or Se) atom and the top site above the Pt-S and Pt-Se bond. Different gas molecule orientations were also considered. The adsorption strength can be assessed using the adsorption energy, defined as $E_a = E_{PtSSe+molecule} - E_{PtSSe} - E_{molecule}$ [17, 33]. Here, $E_{PtSSe+molecule}$ is the total energy of the Janus PtSSe monolayer with the adsorbed gas molecule, and E_{PtSSe} and $E_{molecule}$ are the total energies of the Janus PtSSe monolayer and the gas molecule, respectively. Only the adsorption configurations with the largest adsorption energy were chosen for further discussion, as shown in figure 1 and table 1.

For CO adsorption (figure 1(a)), the CO molecule is above the Pt-Se and Pt-S bond, and the height is 2.60 and 2.77 Å for adsorption on S-layer and Se-layer, respectively. CO_2 molecule lies parallel above two nearby Pt atoms (figure 1(b)) with height of 3.09 and 3.24 Å for adsorption on S-layer and Se-layer, respectively. These large adsorption height suggest CO and CO_2 only form weak physical adsorption on the Janus PtSSe monolayer. H_2O and NH_3 (figures 1(c) and (d)) absorbed above the center of the hexagon with height of 2.24, 2.20 Å for adsorption on S-layer and 2.40, 2.35 Å for adsorption on Se-layer, respectively. Similarly, NO and NO_2 absorbed above the Pt-Se and Pt-S bond, and the height is 1.95 and 2.58 Å for adsorption on S-layer and 2.02, 2.56 Å for adsorption on Se-layer, respectively. The adsorption height indicates that the absorption of H_2O, NH_3, NO and NO_2 molecules on the Janus PtSSe monolayer prefers chemical adsorption. The adsorption strength of last four molecules is much larger than the first two as indicated by the adsorption energies listed in the table 1. More significantly, the E_a of NH_3 molecule adsorption on the S-layer is −0.268 eV and the E_a of NO_2 molecule adsorption on the Se-layer is −0.293 eV, which are much larger than other molecular adsorptions. This makes NH_3 and NO_2 more preferable to be adsorbed on the Janus PtSSe monolayer and can be utilized as selective gas sensor for them.

Gas molecule adsorption would induce charge transfer from substrate and subsequently change the resistivity of the system. Therefore, charge transfer reflects gas sensing ability. This can be visualized using the charge density difference ($\Delta\rho$), which is defined as $\Delta\rho = \rho_{PtSSe+molecule} - \rho_{PtSSe} - \rho_{molecule}$ [17, 33], where $\rho_{PtSSe+molecule}$, ρ_{PtSSe}, and $\rho_{molecule}$ are the charge densities of the Janus PtSSe monolayer with the adsorbed gas molecule, the isolated the Janus PtSSe monolayer, and the isolated gas molecule, respectively. Here, positive (negative) $\Delta\rho$ indicates charge accumulation (depletion). The charge transfer value of gas molecules adsorbed on the Janus PtSSe monolayer is also calculated using the Bader analysis. As shown in figure 2, the charge transfer between CO, CO_2 and H_2O is trivial, no more than 0.03 e. In contrast, the charger transfer for NH_3 molecule adsorption on the S-layer is 0.083 e and for NO_2 molecule adsorption on the Se-layer is 0.176 e, which is much more significant than others. More over, it is found that CO, CO_2, H_2O and NO_2 molecules on the Janus PtSSe monolayer behave like charge acceptors while NH_3 molecule act as the charge donor. Interestingly, NO molecule serves as a donor on the S-layer but as an acceptor on the Se-layer.
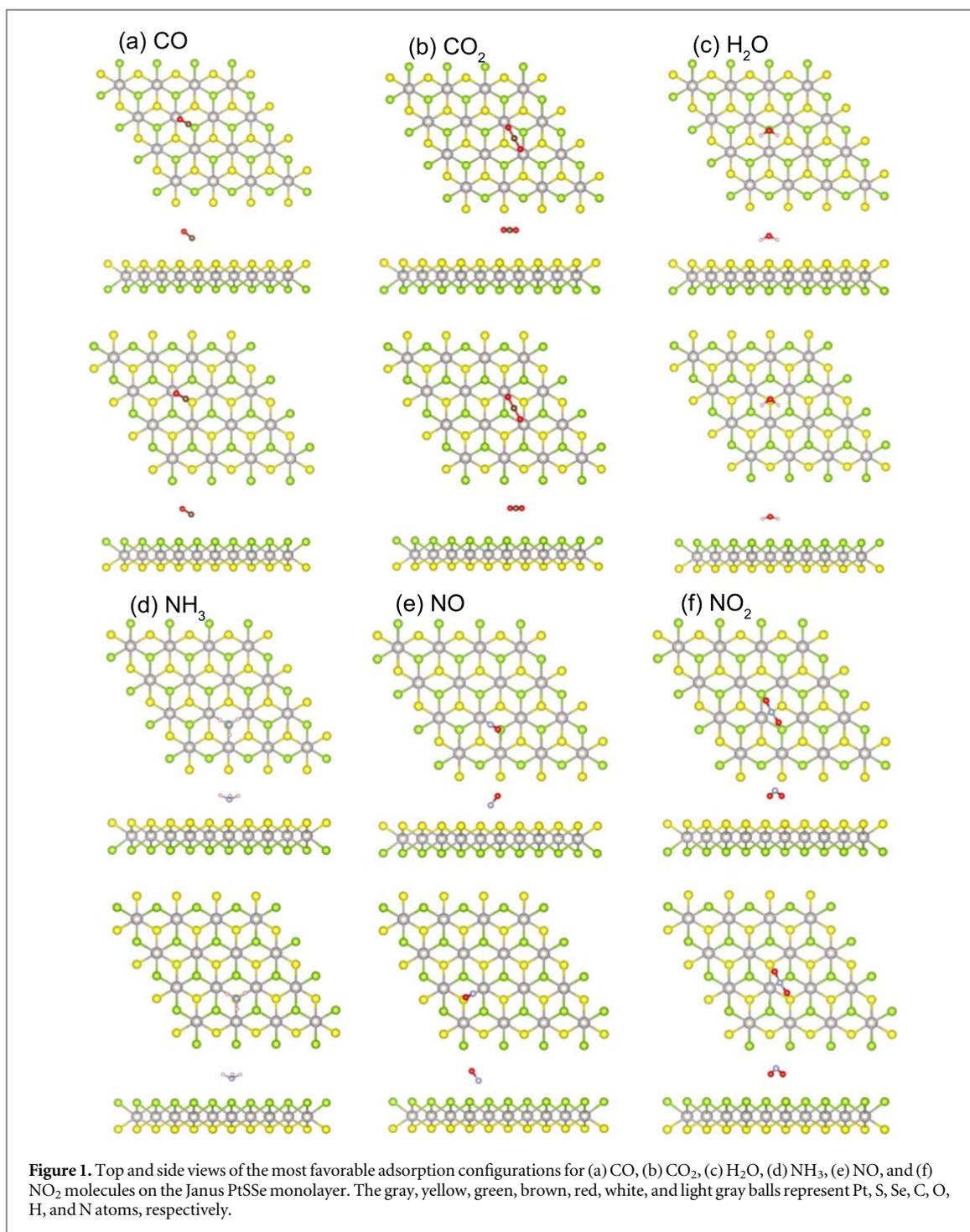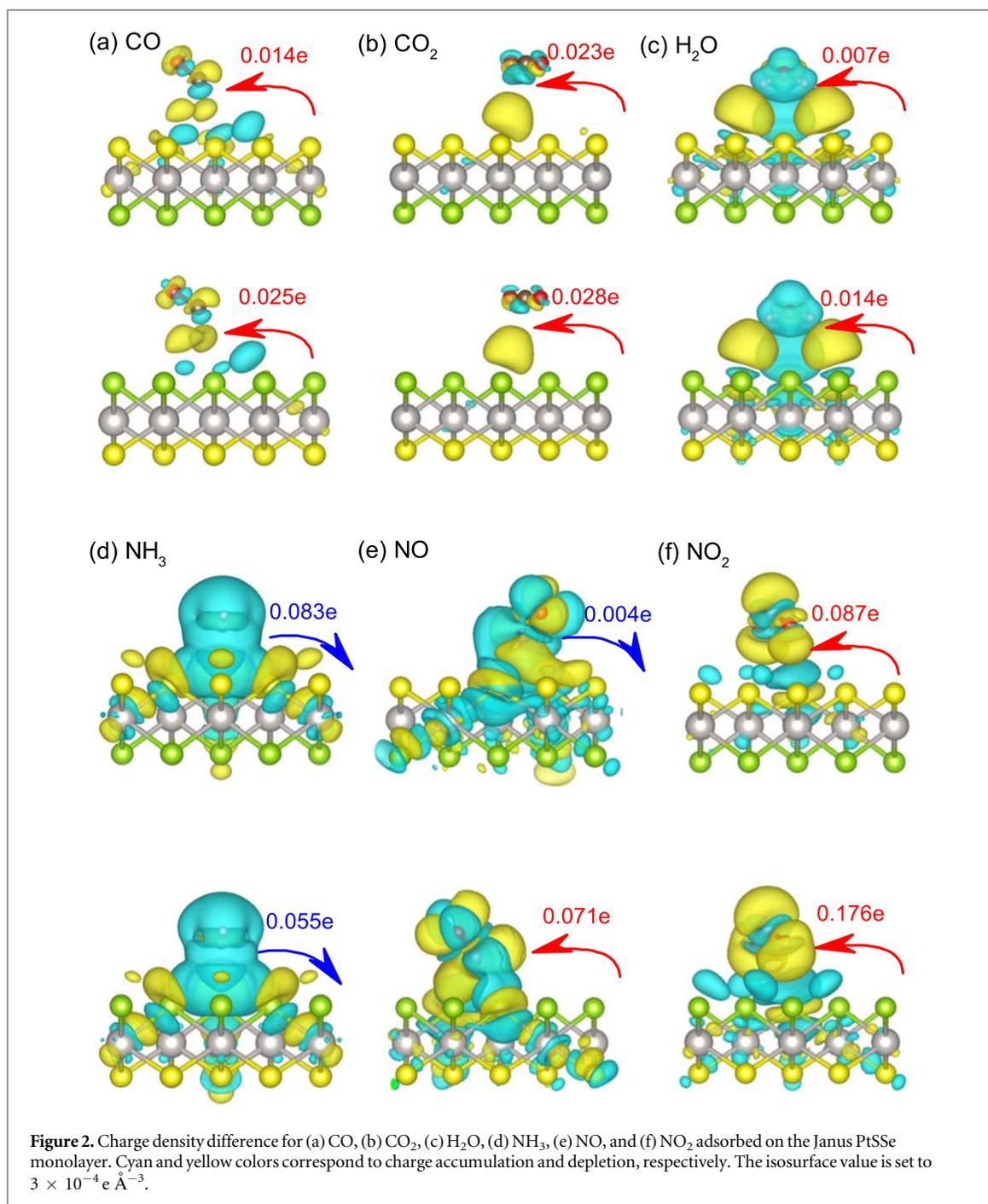
Figure 1. Top and side views of the most favorable adsorption configurations for (a) CO, (b) CO_2, (c) H_2O, (d) NH_3, (e) NO, and (f) NO_2 molecules on the Janus PtSSe monolayer. The gray, yellow, green, brown, red, white, and light gray balls represent Pt, S, Se, C, O, H, and N atoms, respectively.

Table 1. The calculated adsorption heights and adsorption energies (E_a) of gas molecules over the Janus PtSSe monolayer.

	CO	CO_2	H_2O	NH_3	NO	NO_2
Height@S (Å)	2.60	3.09	2.24	2.20	1.95	2.58
Height@Se (Å)	2.77	3.24	2.40	2.35	2.02	2.56
E_a@S (eV)	−0.141	−0.182	−0.202	−0.268	−0.226	−0.241
E_a@Se (eV)	−0.133	−0.180	−0.198	−0.226	−0.211	-0.293

To investigate the effect of strain, adsorption properties were also calculated under biaxial strain, where the strain is defined as $\varepsilon = (a - a_0)/a_0$ with a_0 and a being the lattice constant of the supercell without and with strain, respectively. For simplicity, only NH_3 and NO_2 molecules are selected as representatives. Figure 3 gives

Figure 2. Charge density difference for (a) CO, (b) CO_2, (c) H_2O, (d) NH_3, (e) NO, and (f) NO_2 adsorbed on the Janus PtSSe monolayer. Cyan and yellow colors correspond to charge accumulation and depletion, respectively. The isosurface value is set to 3×10^{-4} e Å^{-3}.

the adsorption heights and adsorption energies under the strain modulation. The calculated results suggest that adsorption strength can be enhanced by applying biaxial strain. It is also found that the NO_2 molecule adsorption is more sensitive to the applied strain. Both molecules are found to have more tunable adsorption strength on the Se-layer.

Charge transfer between molecules and substrates has an influence on the performance of a gas sensor. Therefore, it is important to understand the effect of external electric field on the charge transfer. Figure 4(a) shows the schematic illustration of the applied electric field, which is perpendicular to the Janus PtSSe monolayer with the positive direction pointing upward. Figure 4(b) gives the variation of the charge transfer of NH_3 and NO_2 molecules with respect to the electric field. It is found that the charge transfer from the substrate to the molecules increases with the increment of the applied electric field strength along the positive direction. When a reverse electric field is applied, the charge transfer decreases. It is also revealed that the charge transfer of NO_2 molecule is much more than that of NH_3. This charge transfer modulation under external electric field can be attribute to the dipole moment in the molecule-based system [41]. This modulation of charge transfer under electric field renders the Janus PtSSe monolayer as a perfect candidate for tunable gas sensor with electric field.
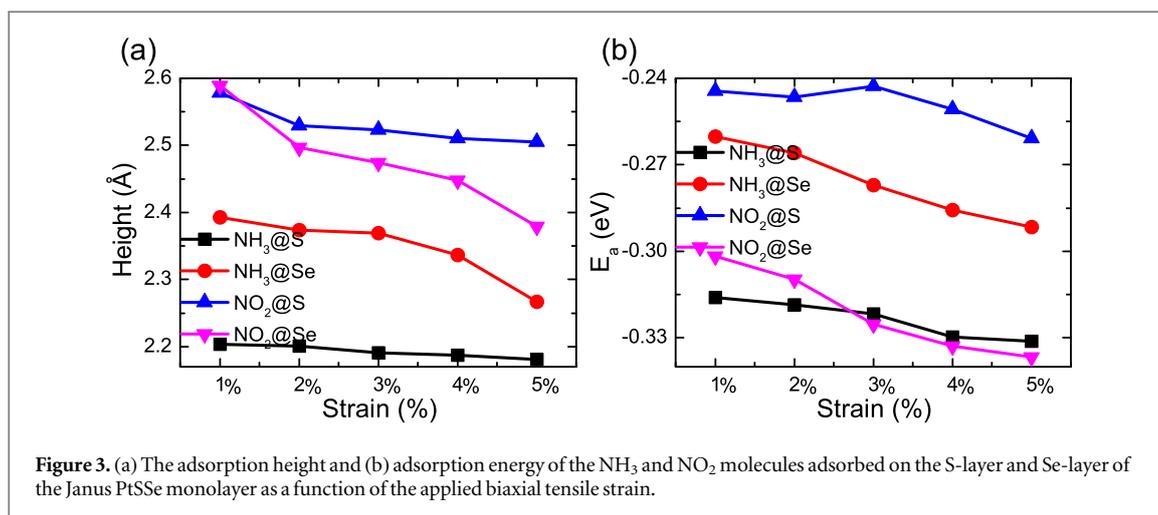
Figure 3. (a) The adsorption height and (b) adsorption energy of the NH_3 and NO_2 molecules adsorbed on the S-layer and Se-layer of the Janus PtSSe monolayer as a function of the applied biaxial tensile strain.
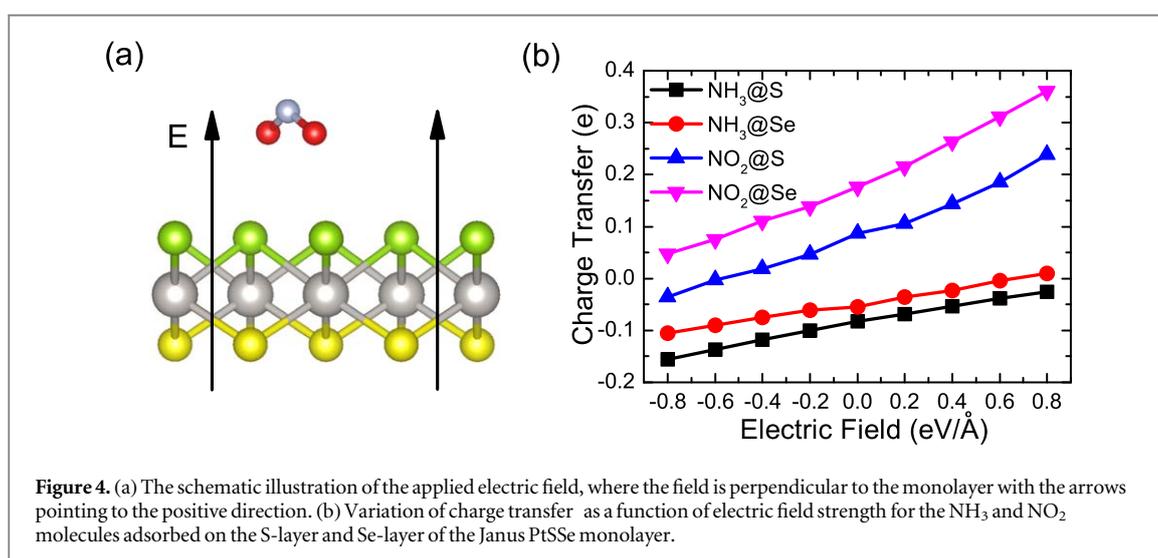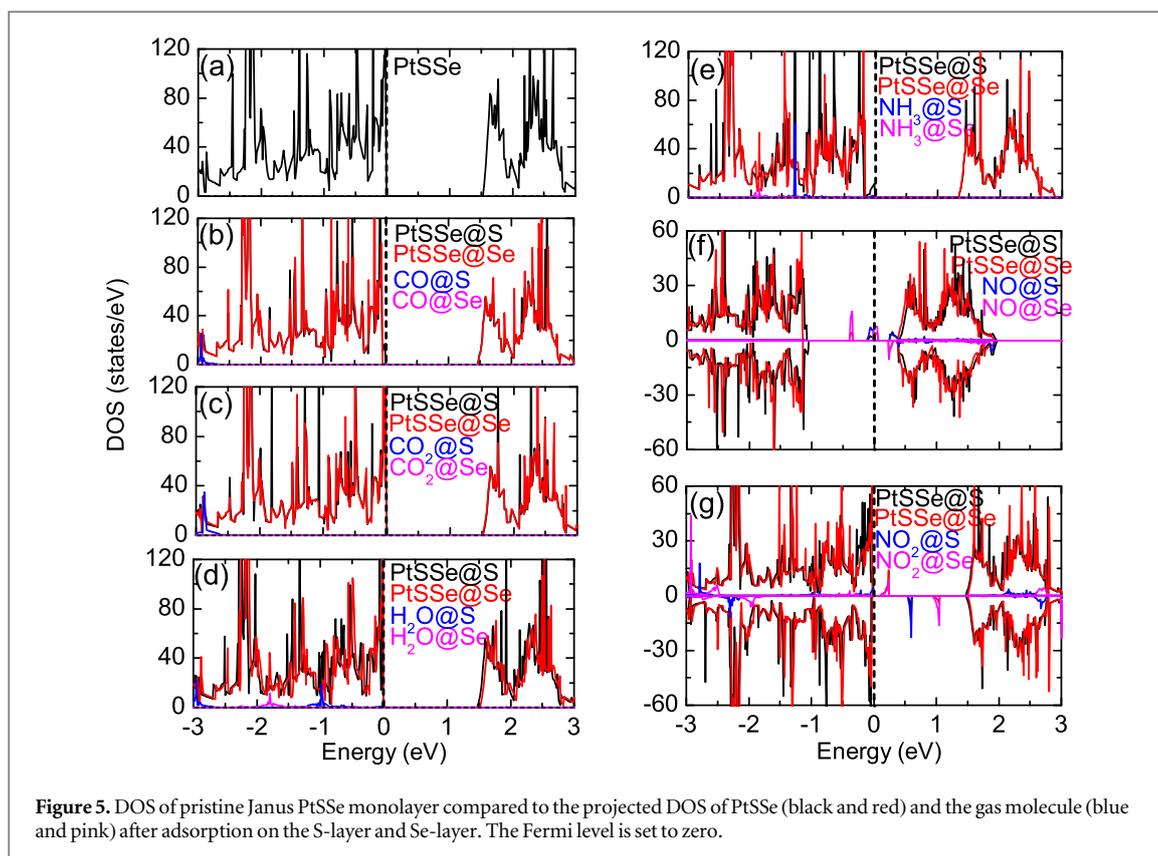

Figure 4. (a) The schematic illustration of the applied electric field, where the field is perpendicular to the monolayer with the arrows pointing to the positive direction. (b) Variation of charge transfer as a function of electric field strength for the NH_3 and NO_2 molecules adsorbed on the S-layer and Se-layer of the Janus PtSSe monolayer.

Gas sensing ability relies heavily on the electronic properties of the Janus PtSSe monolayer after molecules adsorption. The density of states (DOS) of the molecules and substrate are provided in figure 5. Our calculated band gap for the Janus PtSSe monolayer is 1.5 eV. It is shown that the adsorption of CO, CO_2, H_2O gas molecules does not change the band gap. The induced molecular states are far away from the Fermi level, which would hardly influence the electronic properties. For the NH_3 adsorption, there is a downward shifting of the valence band for Se-layer adsorption, which changes the band gap. Due to the unpaired electrons, asymmetric magnetic states are induced when NO and NO_2 molecules are adsorbed on the Janus PtSSe monolayer. The induced impurity states are in the band gaps near Fermi level, which would alter the electronic properties significantly. It is also observed that the position of the energy states induced by molecule adsorption on S-layer and Se-layer are different, which suggests the possibilities of designing a selective gas sensor using different adsorption layer of the Janus PtSSe monolayer.

Compared with the first proposed Janus MoSSe gas sensor, our Janus PtSSe monolayer has better sensing properties. For CO, CO_2, NH_3, NO, and NO_2 adsorption on the Se-layer, the adsorption energies are -0.133 eV, -0.180 eV, -0.226 eV, -0.211 eV, and -0.293 eV for Janus PtSSe, which are comparable or larger than -0.136 eV, -0.182 eV, -0.200 eV, -0.158 eV, and -0.249 eV for Janus MoSSe [33]. The charge transfer for above mentioned adsorptions are 0.025 e, 0.028 e, 0.055 e, 0.071 e, and 0.176 e for Janus PtSSe, which are also much larger than 0.015 e, 0.024 e, 0.031e, 0.038 e, and 0.107 e for Janus MoSSe [33]. This increased sensing properties can be attributed to the crucial role of the d electrons in the transitional metal and the fact that there are more valence electrons in PtSSe than in MoSSe [17].

Figure 5. DOS of pristine Janus PtSSe monolayer compared to the projected DOS of PtSSe (black and red) and the gas molecule (blue and pink) after adsorption on the S-layer and Se-layer. The Fermi level is set to zero.

4. Conclusion

In conclusion, the gas sensing properties of the Janus PtSSe monolayer for CO, CO_2, H_2O, NH_3, NO and NO_2 are investigated using first-principles calculations. Our results suggest that CO and CO_2 only form weak physical adsorption whereas the absorption of H_2O, NH_3, NO and NO_2 molecules on the Janus PtSSe monolayer prefers chemical adsorption. CO, CO_2, H_2O and NO_2 molecules draw charge from the Janus PtSSe monolayer whereas NH_3 acts as charge donor. Interestingly, NO donates charge when adsorbed on S-layer but accept charge when adsorbed on Se-layer. Biaxial tensile strain is found to be able to enhance the adsorption strength for NH_3 and NO_2. It is also found that the charge transfer can be consistently modified by applying a perpendicular electric field. The DOS results show gap states near Fermi level can be induced with adsorption of NO and NO_2 molecules. Our theoretical findings indicate that the Janus PtSSe monolayer is a promising gas sensor with superior and tunable sensing properties.

Acknowledgments

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