Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

Monolayer GeS as a potential candidate for NO_2 gas sensors and capturers

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The energetic stability can be determined by the definitions as follows. Firstly, the adsorption energy of molecule (E_{ad}^{mol}) on single-layer GeS covered with water molecules is computed by Eq.(1).

$$E_{ad}^{mol} = E_{mol+water} - E_{water} - E_{molecule} \quad (1)$$

Here, $E_{mol+water}$, E_{water}, $E_{molecule}$ are the total energies of molecule and water co-adsorbed, water adsorbed on GeS nanosheet, and free molecule placed in a large cubic box, respectively. Similarly, the adsorption energy of oxygen atom on pristine GeS monolayer is calculated by Eq.(2).

$$E_{O_{ad}} = E_{O-ad} - E_{pristine} - 0.5 * E_{O_2} \quad (2)$$

The formation energy of S-vacancy (E_{S_V}) and oxygen atom doping in the S-vacancy ($E_{O_{sub}}$) on GeS is defined as Eq.(3) and Eq.(4), respectively,

$$E_{S_V} = E_{S-vac} + E_S - E_{pristine} \quad (3)$$

$$E_{O_{sub}} = E_{O-sub} + E_S - E_{pristine} - 0.5 * E_{O_2} \quad (4)$$

where E_{O-ad}, $E_{pristine}$, E_{S-vac} and E_{O-sub} denote the total energies of O-adsorbed, pristine, single S-vacancy, and O-doped in S-vacancy GeS nanosheets, respectively. E_{O_2} and E_S represents the energies of free O_2 molecule and one S atom in free S_8 molecule,[1] respectively.

Besides, the recovery time (τ) upon gas molecule adsorption is

defined with $\tau = \omega^{-1} \exp(\frac{E^*}{K_B T})$,[2,3] on the basis of the conventional transition state theory. Here, T denotes the temperature, K_B the Boltzmann' constant, ω the attempt frequency (10^{-13} s^{-1}) and E^* the desorption energy barrier of gas molecule (approximated as the absolute of adsorption energy).

Table S1 Calculated lattice parameters of unit cell (a, b), average length of Ge−S ($d_{Ge–S}$) bonds, and band-gap energy (E_{gap}) of GeS monolayer. (* denotes the calculations at the HSE06 level).

Monolayer GeS	a, b (Å)	$d_{Ge–S}$(Å)	E_{gap} (eV)
This work	4.38, 3.67	2.415, 2.471	1.604, 2.166*
Ref. 4	4.33, 3.67	2.48	2.34*
Ref. 5	4.45, 3.64	2.42, 2.46	-
Ref. 6	4.48, 3.62	-	1.23
Ref. 7	4.40, 3.69	-	-
Ref. 8	3.66, 4.50	2.42, 2.48	1.58, 2.42*
Ref. 9	3.64, 4.50	2.43, 2.46	1.73, 2.43*

Table S2 Calculated adsorption energies (E_{ads}) for NH_3, SO_2 and NO_2 on monolayer GeS at different coverages, along with that obtained without vdW.

E_{ads} (eV) / Super cell	Adsorbate			Concentration
	NH_3	SO_2	NO_2	Molecules/nm^2
3×3	-0.357	-0.442	-0.788	0.691
4×4	-0.367	-0.400	-0.791	0.389
5×5	-0.277	-0.446	-0.798	0.249
Without vdW				
3×3	-0.199	-0.198	-0.638	0.691

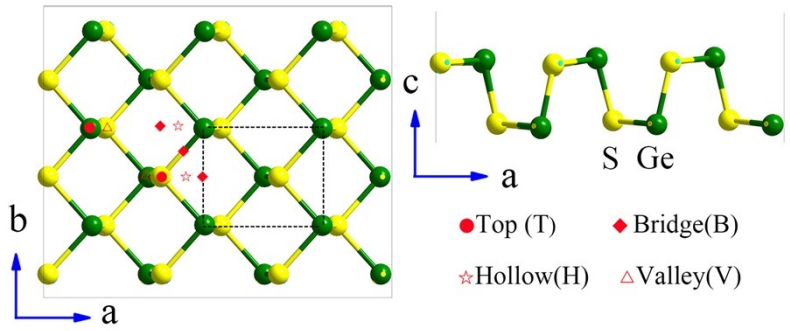

Fig. S1 A schematic illustration of the structure of pristine GeS monolayer and the adsorption sites of molecules on it.

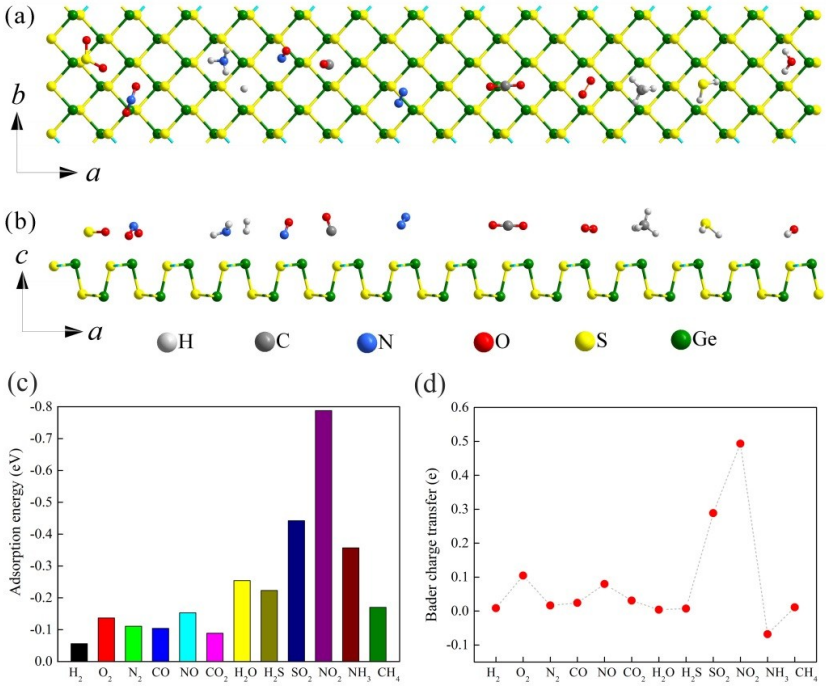

Fig. S2 The most stable adsorption configurations (a, b), computated adsorption energies (c) and the Bader charge transfer (d) for various molecules on GeS monolayer.

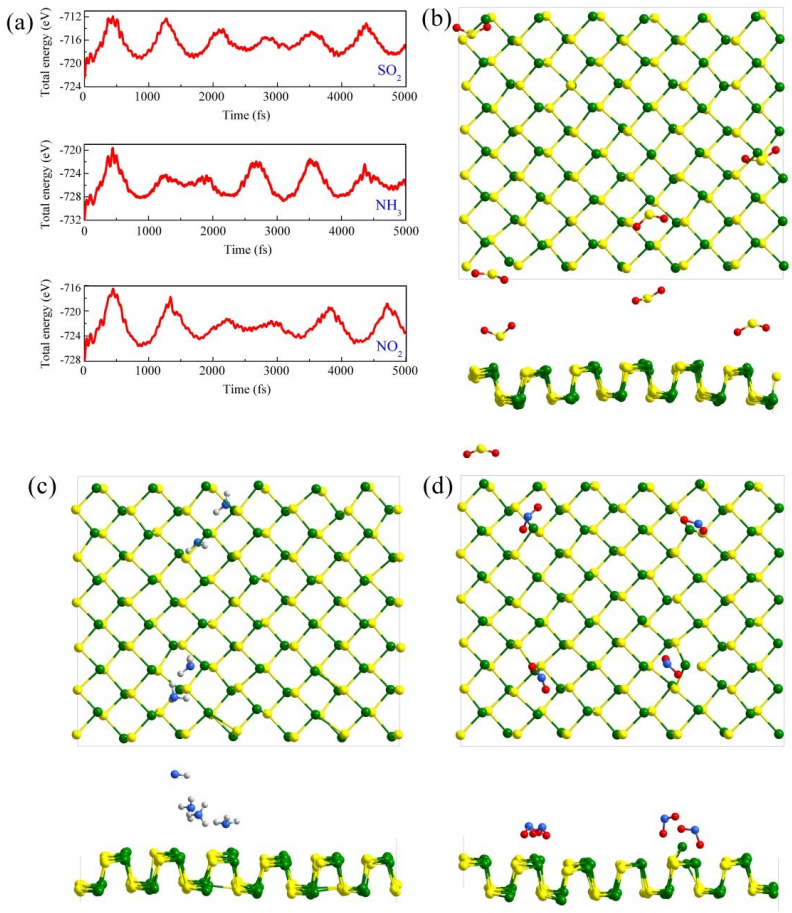

Fig. S3 Results for molecular dynamics simulations performed at 300 K for 5 ps. (a) Total energy fluctuations with time; (b, c, d) the final adsorption configurations for SO_2, NH_3 and NO_2 on GeS monolayer achieved after 5 ps, respectively.

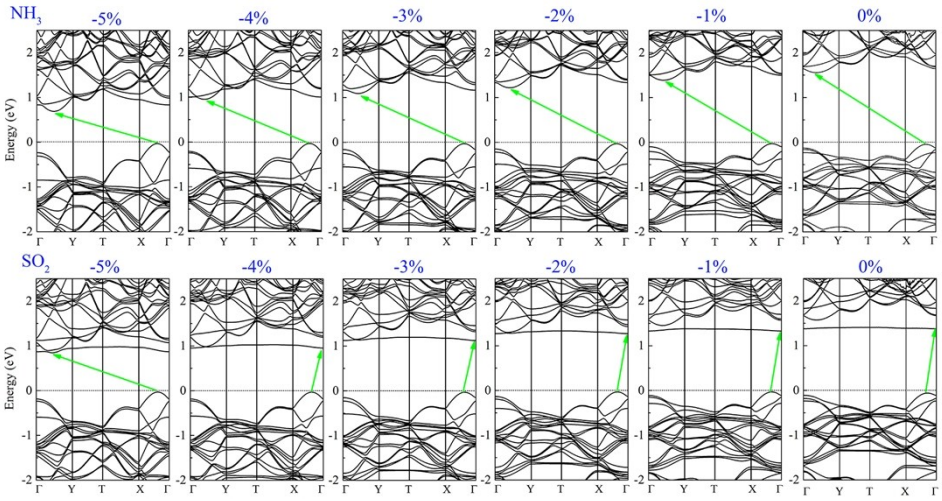

Fig. S4 The band structures of NH_3 and SO_2 absorbed on GeS with the various compressive strains.

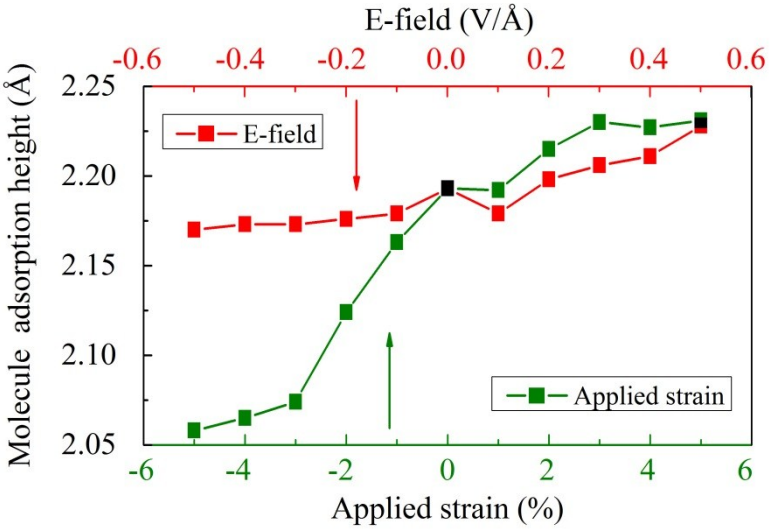

Fig. S5 The adsorption height of NO_2 adsorbed on GeS varying with the applied strains and E-fields, respectively.

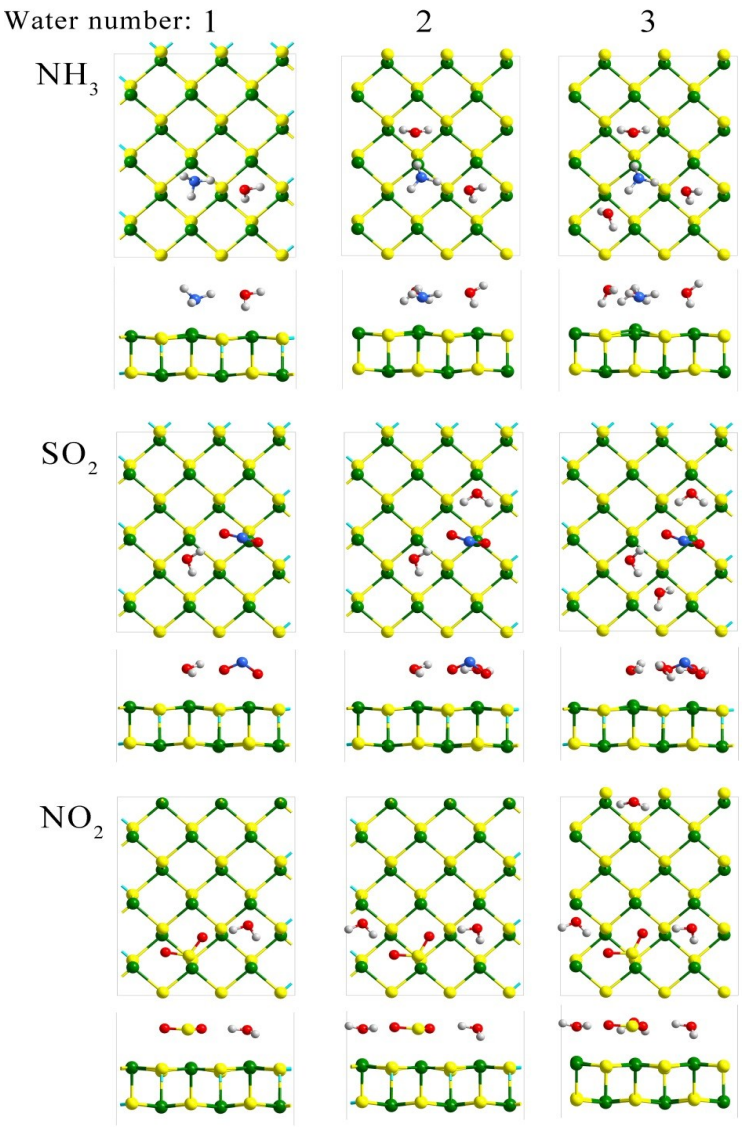

Fig. S6 An illustration of the favorable configurations for NH_3, SO_2 and NO_2 adsorbed on monolayer GeS covered by water molecules ranging from one to three.

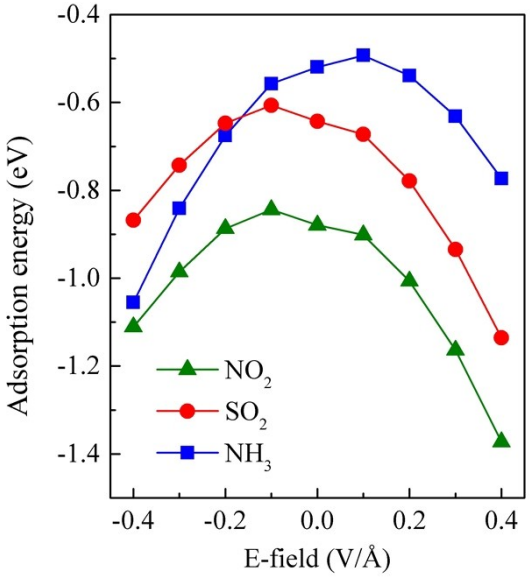

Fig. S7 Calculated adsorption energies varying with the external E-field for NH_3, SO_2 and NO_2 adsorbed on monolayer GeS covered by one water molecule, respectively.

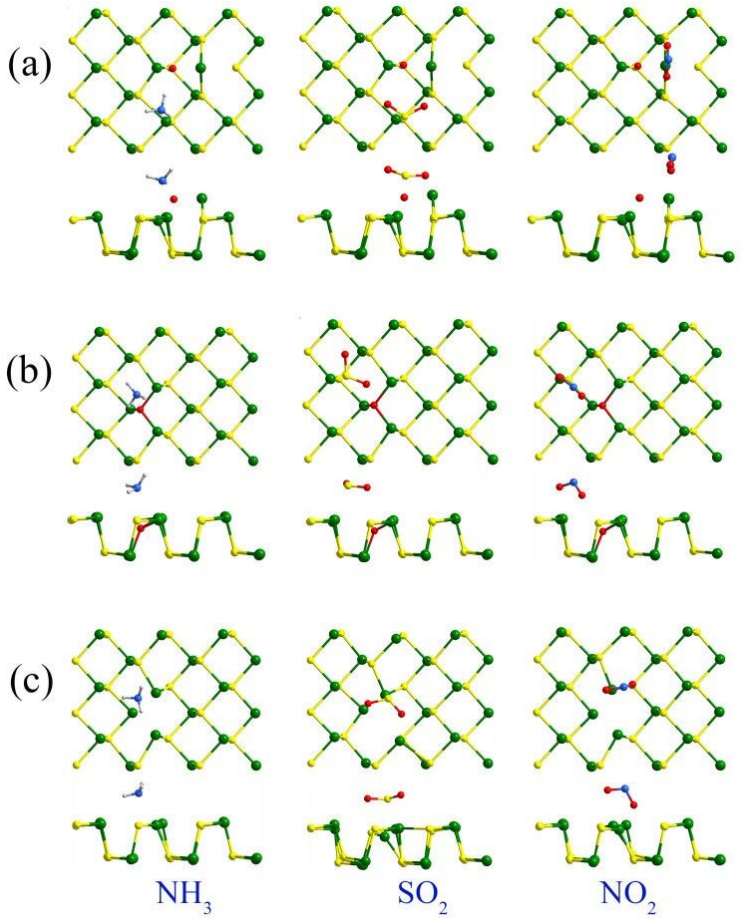

Fig. S8 Adsorption configurations of NH_3, SO_2 and NO_2 on defective GeS nanosheets, (a) O-adsorbed GeS, (b) O-doped GeS, (c) S-vacancy GeS.

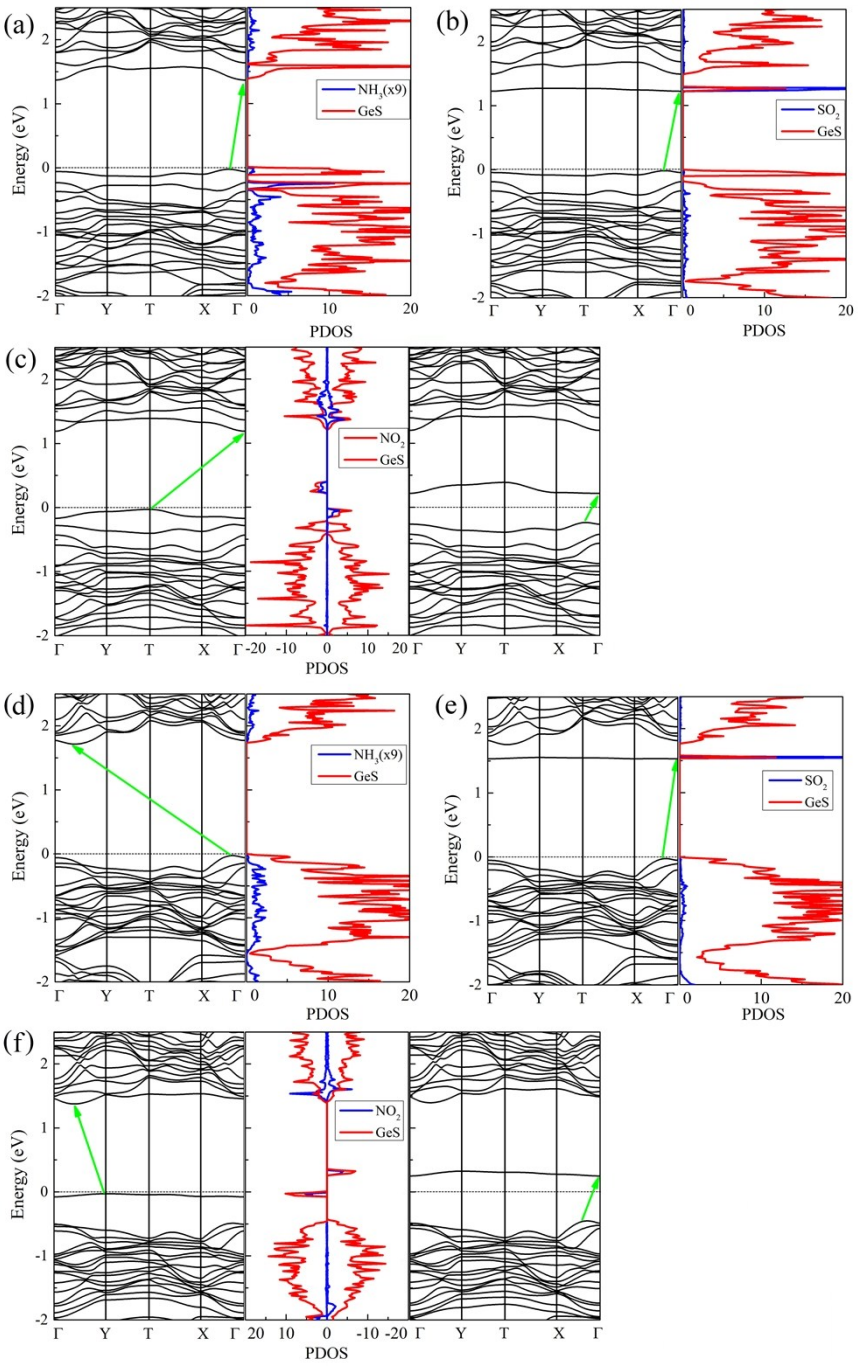

Fig. S9 The band structures and total DOS for NH_3, SO_2, and NO_2 adsorbed on O-adsorbed (a-c) and O-doped (d-f) GeS sheets, respectively. The Fermi energy (dashed line) is set at zero. In the NO_2 cases, the left and right panels are spin-up and spin-down states, respectively.

Video S1: A movie simulated by AIMD for NH_3 adsorbed on GeS at 300 K for 5 ps.

Reference

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