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Supplementary Information

Black arsenene as a promising anisotropic sensor with high sensitivity and selectivity: insights from a first-principles investigation

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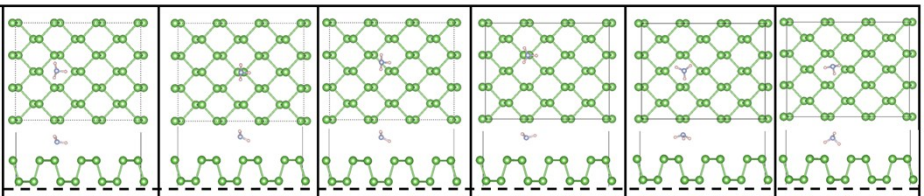
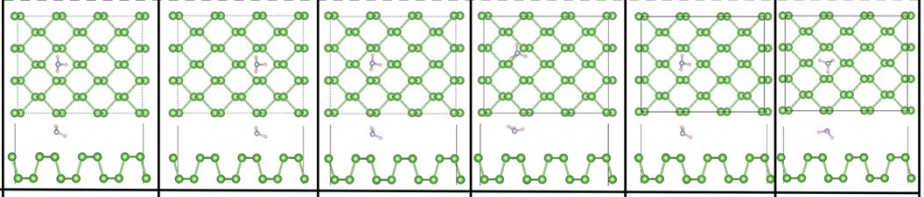
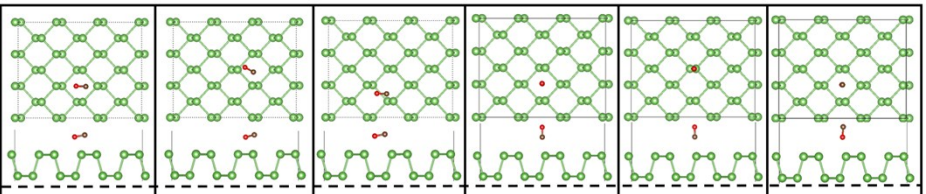
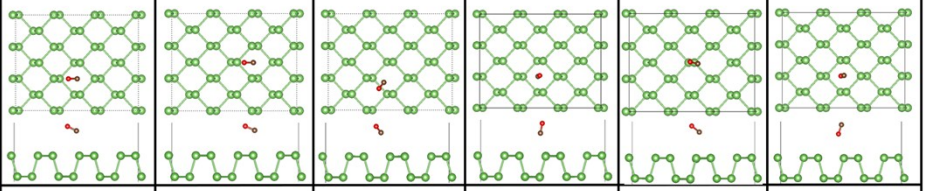
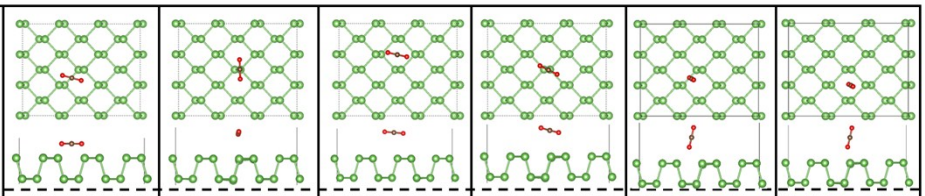
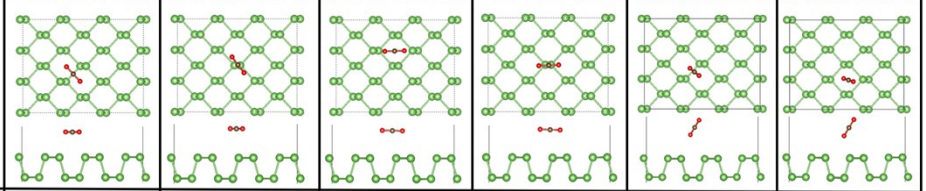
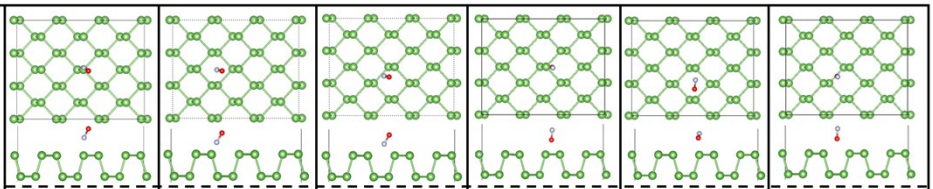
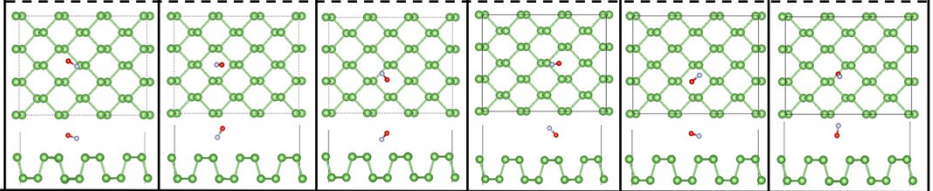
(a) NH_3							
Initial configuration	Top view						
	Side view						
Configuration after structural optimizaiton	Top view						
	Side view						
⊿E(eV)		0	0	0.003	0.054	0	0.055

(b) CO							
Initial configuration	Top view						
	Side view						
Configuration after structural optimizaiton	Top view						
	Side view						
⊿E(eV)		0	0.001	0.01	0.038	0.05	0.088

(c) CO_2							
Initial configuration	Top view						
	Side view						
Configuration after structural optimizaiton	Top view						
	Side view						
⊿E(eV)		0	0.049	0.038	0.051	0.11	0.115

(d) NO							
Initial configuration	Top view						
	Side view						
Configuration after structural optimizaiton	Top view						
	Side view						
⊿E(eV)		0	0.157	0.089	0.25	0.094	0.25

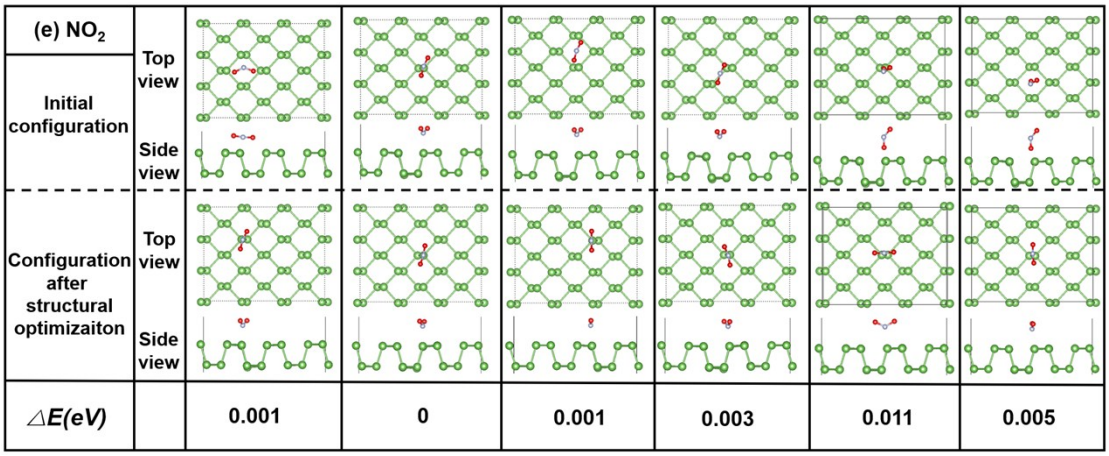
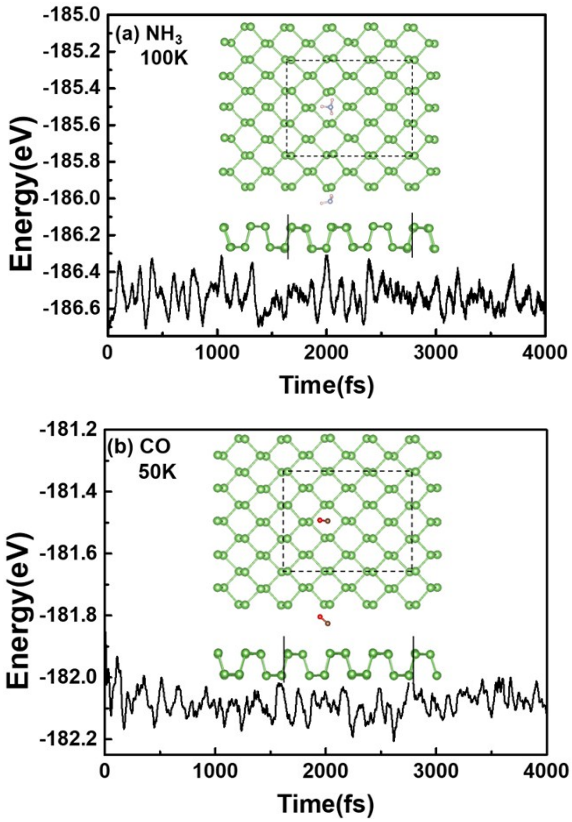


Figure S1 Possible adsorption configurations before and after structural optimizations. Several typical orientations of gas molecules with respect to black arsenene are considered. Relative energy differences (ΔE) with respect to the preferred adsorption configuration are also given for comparison. The green, cyan, pink, red, and brown spheres represent As, N, H, O, and C atoms, respectively.



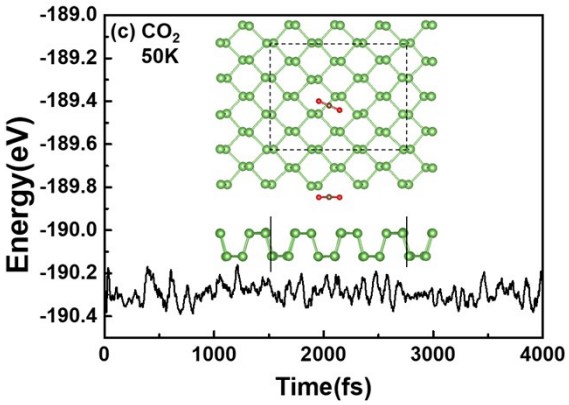


Figure S2. Total energy fluctuations of the adsorptions of (a) NH_3, (b) CO, and (c) CO_2 on B-As at specific temperatures. Insets are the snapshots of molecular dynamics simulations at 4 ps.

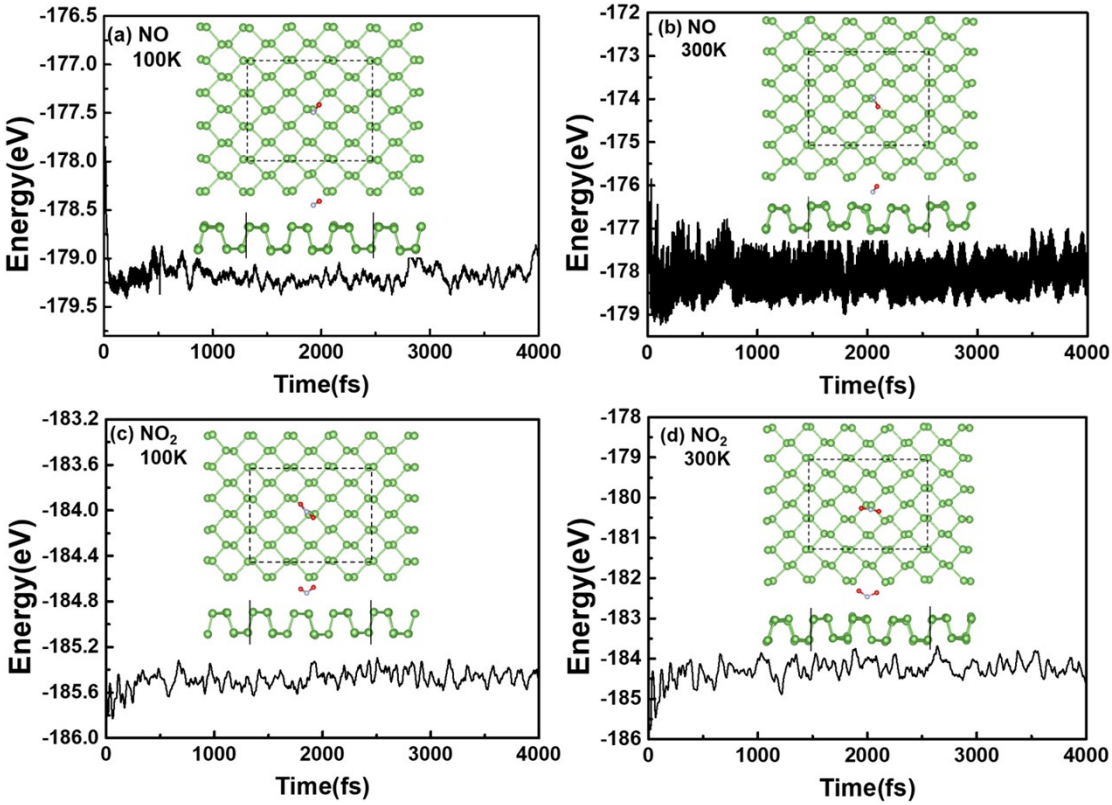


Figure S3. Total energy fluctuations of the adsorptions of NO (a, b) and NO_2 (c, d) on B-As at different temperatures. Insets are the snapshots of molecular dynamics simulations at 4 ps.

Ab-initio molecular dynamics simulations (AIMD) adopting the canonical (NVT) ensemble were performed with a time step of 1 fs for a total simulation time of 4 ps at various temperatures. At low temperatures (e.g., 50 K), all gas molecules can sustain their adsorption positions as shown in Fig. 1 of the manuscript. Higher temperature (e.g., 300 K) may induce desorption of CO, CO_2, and NH_3, of which the adsorption strengths on B-As are low. However, NO and NO_2, which have higher adsorption strengths, can still maintain their favor adsorption positions at 300 K (see **Figure S2**

and **S3)**.

Table S1 Adsorption energies (E_{ads}) (eV) corresponding to the most favored configurations as calculated using different vdW correction methods.

	NH_3	CO	CO_2	NO	NO_2
E_{ads} (eV)-vdW-D2	-0.26	-0.14	-0.16	-0.33	-0.34
E_{ads} (eV)-vdW-D3	-0.24	-0.14	-0.16	-0.32	-0.33

From the conventional transition state theory, the recovery time can be expressed as $\tau = \omega^{-1}\exp(-E_{ad}/k_BT)$[1], where T is temperature, k_B is Boltzmann's constant, and ω is the attempt frequency. If ω is taken as 10^{13} s^{-1} [2], the recovery time at room temperature (300 K) of these gas molecules on B-As is estimated.

Table S2 Recovery time of gas molecules adsorbed on B-As at room temperature.

	NH_3	CO	CO_2	NO	NO_2
E_{ad} (eV)	-0.26	-0.14	-0.16	-0.33	-0.34
τ (s)	2.33×10^{-9}	2.24×10^{-9}	4.87×10^{-11}	3.49×10^{-8}	5.14×10^{-8}

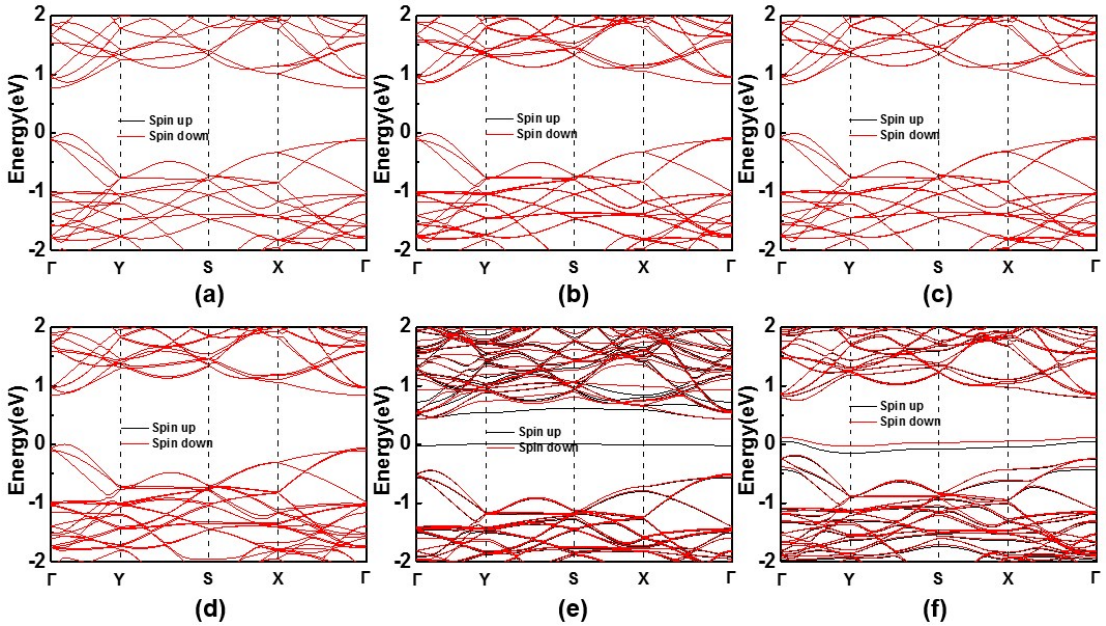


Figure S4. Spin-polarized band structures of pure black arsenene (a), and CO (b), CO_2 (c), NH_3 (d), NO (e), and NO_2 (f) adsorbed B-As. Fermi level is located at 0 eV.

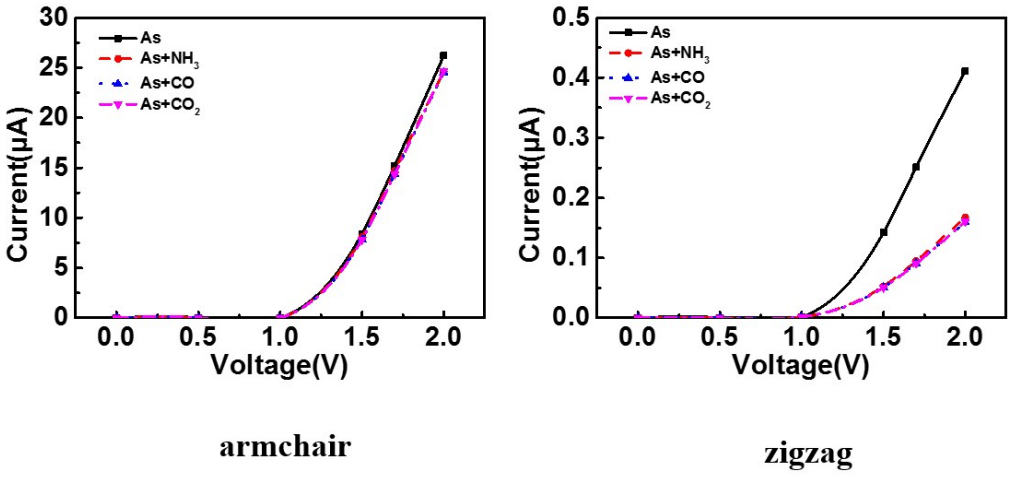


Figure S5. *I-V* curves (half of total current) of black arsenene before and after the adsorptions of NH_3, CO, and CO_2.

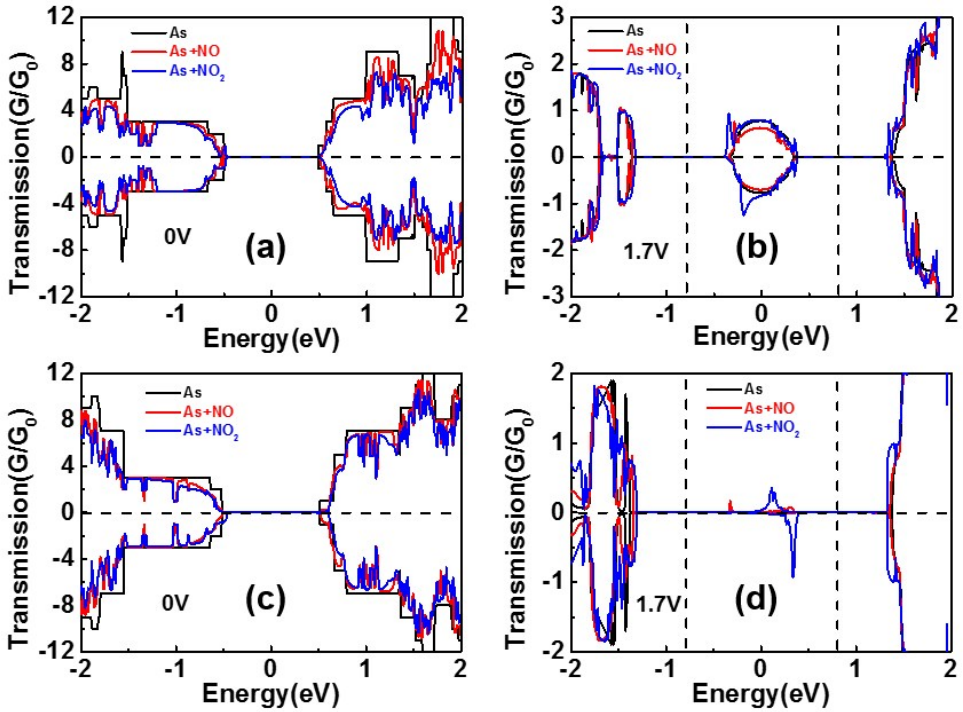


Figure S6. Spin-polarized transmission spectra of black arsenene before and after the adsorptions of NO and NO_2 along the armchair (a, b) and zigzag (c, d) directions. The vertical dashed lines in (b) and (d) denote the bias windows.

Reference

1.Y.H. Zhang, Y.B. Chen, K.G. Zhou, C.H. Liu, J. Zeng, H.L. Zhang and Y. Peng, *Nanotechnology*, 2009, **20**, 185504.

2.A. Kokalj, *Corros. Sci.*, 2013, **68**, 195-203.