Supporting Information

Metal-Modified C$_3$N$_1$ Monolayer Sensors for Battery Instability Monitoring

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Table of Contents

Computational section
Details of thermodynamic calculation
Details of diffusion performance calculation
Figure S1. The energy fluctuations with time process for the *ab initio* molecular dynamics of Cu/Ag-C_2N_1 monolayer.
Figure S2. Electrostatic potential and work function of (a) the Cu-C_2N_1 and (b) the Ag-C_2N_1 monolayer.
Figure S3. Adsorption structures of C_2H_4 at different sites on the Ag-C_2N_1.
Figure S4. Adsorption structures of C_2H_6 at different sites on the Ag-C_2N_1.
Figure S5. Adsorption structures of H_2O at different sites on the Ag-C_2N_1.
Figure S6. Adsorption structures of NH_3 at different sites on the Ag-C_2N_1.
Figure S7. Adsorption structures of NO_2 at different sites on the Ag-C_2N_1.
Figure S8. Adsorption structures of PF_5 at different sites on the Ag-C_2N_1.
Figure S9. Adsorption structures of C_2H_4 at different sites on the Cu-C_2N_1.
Figure S10. Adsorption structures of PF_5 at different sites on the Cu-C_2N_1.
Figure S11. Adsorption structures of C_2H_6 at different sites on the Cu-C_2N_1.
Figure S12. Adsorption structures of NH_3 at different sites on the Cu-C_2N_1.
Figure S13. Adsorption structures of H_2O at different sites on the Cu-C_2N_1.
Figure S14. Adsorption structures of NO_2 at different sites on the Cu-C_2N_1.
Figure S15. The initial adsorption configuration of gases (PF_5, NO_2, NH_3, H_2O, C_2H_4, and C_2H_6) on the Ag-C_2N_1.
Figure S16. The initial adsorption configuration of gases (PF_5, NO_2, NH_3, H_2O, C_2H_4, and C_2H_6) on the Cu-C_2N_1.
Figure S17. The COHP between gases (C_2H_4, PF_5, C_2H_6, H_2O, NH_3, and NO_2) and the Ag-C_2N_1.
Figure S18. The COHP between gases (C_2H_4, PF_5, C_2H_6, H_2O, NH_3, and NO_2) and the Cu-C_2N_1.
Figure S19. DOS and PDOS of (a) C_2H_4, (b) C_2H_6, (c) PF_5, (d) H_2O, (e) NH_3, (f) NO_2 on the Ag-C_2N_1 monolayer.
Figure S20. DOS and PDOS of (a) C_2H_4, (b) C_2H_6, (c) PF_5, (d) H_2O, (e) NH_3, (f) NO_2 on the Cu-C_2N_1 monolayer.
Figure S21. The initial and the final stable configurations of gas on the Ag-C_2N_1. (a) NH_3, (b) H_2O, (c) PF_5, (d) C_2H_6, (e) C_2H_4, and (f) NO_2.
Figure S22. The initial and the final stable configurations of gas on the Cu-C_2N_1. (a) NH_3, (b) H_2O, (c) PF_5, (d) C_2H_6, (e) C_2H_4, and (f) NO_2.
Figure S23. The stable configurations of NO_2 on the Ag-C_2N_1 at different

temperatures. (a) 300 K, (b) 400 K, (c) 500 K, (d) 600 K, and (e) 700 K.

Figure S24. The stable configurations of NO_2 on the Cu-C_2N_1 at different temperatures. (a) 300 K, (b) 400 K, (c) 500 K, (d) 600 K, (e) 700 K, and (f) 800 K.

Table S1. The amount of charge transferred by the gas adsorbed.

Table S2. Diffusion coefficient of six gases on the Cu/Ag-C_2N_1 monolayer at 300 K

Table S3. Diffusion coefficients of NO_2 on the Cu/Ag-C_2N_1 at different temperatures.

Table S4. The recovery time (s) of the gas on the Cu-C_2N_1.

Table S5. The recovery time (s) of the gas on the Ag-C_2N_1.

References

Computational section

For the original C_3N_1, Ag-C_2N_1, Cu-C_2N_1, PF_5, NO_2, NH_3, H_2O, C_2H_4, and C_2H_6, all structural optimization and electronic performance calculations are performed using DFT, based on Dmol^3 code [1] under the Perdew-Burke-Ernzerhof functional, gradient approximation method correlation [2, 3], double precision number basis set polarization function is used to process atomic orbitals. The dispersion-corrected DFT method was selected based on Grimme vdW correction [4], which can accurately describe the interaction in all weak calculations. The global cut-off radius of real space is 4.9 Å, and the Monkhorst−Pack scheme is used to sample $3 \times 2 \times 1$ k points in the Brillouin area to complete high-quality theoretical evaluation. In addition, the convergence tolerance of geometry optimization is 1×10^{-5} Ha for the total energy, 0.002 Ha/Å for the atomic force, and 0.005 Å for the highest displacement, respectively. The electron distribution and charge transfer were calculated using the Mulliken method [5]. To eliminate interactions between periodic images, use a 20 Å vacuum layer vertically to the Cu/Ag-C_2N_1 monolayer. The C-N bond length is 1.41 Å, the C-C bond length is 1.43 Å, and the maximum spacing of C-N-C-C is 2.83 Å in the initial C_3N_1 monolayer.

Details of thermodynamic calculation

These mainly include enthalpy, entropy, and the Gibbs free energy.

First, enthalpy (H) is calculated by

$$H = H_{trans} + H_{rot} + H_{vib} + RT$$

$$= \frac{R}{2k}\sum_i hv_i + \frac{R}{k}\sum_i \frac{hv_i exp(-hv_i/kT)}{[1 - exp(hv_i/kT)]^2} + 4R \tag{1}$$

where H_{trans}, H_{rot} and H_{vid} are the translation enthalpy, rotation enthalpy, and vibration enthalpy (kcal/mol), respectively. R and T are the ideal gas constant (8.314 J/mol/K) and the absolute temperature (K), accordingly. k is the Boltzmann constant, h is Planck's constant, and v_i, is the vibrational frequency.

Second, entropy (S) is given by

$$S = S_{trans} + S_{rot} + S_{vib}$$

$$= \frac{5}{2}RlnT + \frac{5}{2}Rlnw - \frac{5}{2}lnp - 2.3482$$

$$+ \frac{R}{2}ln\left[\frac{\pi}{\sqrt{\sigma}}\frac{8\pi^2 cl_A}{h}\frac{8\pi^2 cl_B}{h}\frac{8\pi^2 cl_C}{h}\left(\frac{kT}{hc}\right)^3\right]$$

$$+ \frac{3}{2}R + R\sum_i \frac{hv_i/kT\ exp(-hv_i/kT)}{1 - exp(-hv_i/kT)}$$

$$- R\sum_i \ln\left[1 - exp(-hv_i/kT)\right] \tag{2}$$

Where S_{trans}, S_{rot}, and S_{vid} are the translation, rotation, and vibration entropies (cal/mol/K), accordingly. w is the molecular mass, p is the pressure, σ is the symmetry number, c is the molar concentration of the molecules, and $I_{A\ (B,\ C)}$ is the moment of inertia.

Finally, the Gibbs free energy (G) (kJ/mol) is defined as

$$G = E(OK) + H - T \cdot S \tag{3}$$

where E (0 K) is the zero-point energy (kcal/mol).

Details of diffusion performance calculation

From the point of view of gas motion (diffusion), the main energy barrier to be overcome in NO_2 adsorption on the $Ag-C_2N_1$ and $Cu-C_2N_1$ monolayer was the gas diffusion energy barrier. The diffusion activation energy can be obtained by calculating the gas motion parameters according to molecular dynamics simulation with our previous work [6], and by this means, the energy barrier of NO_2 adsorption on the $Cu/Ag-C_2N_1$ monolayer can be well verified. Therefore, the mean-squared displacement (MSD) and diffusion coefficients (Ds) were used to investigate the diffusion properties of gases according to the Einstein diffusion law; these quantities were computed by the following equations.

$$MSD(t) = \frac{1}{N} \sum_{i=1}^{N} \left\langle \left| r_i(t) - r_i(0) \right|^2 \right\rangle \tag{4}$$

$$D_S = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \sum_{i}^{n} \left\langle \left| r_i(t) - r_i(0) \right|^2 \right\rangle \tag{5}$$

where N is the number of molecules, $r_i(t)$ is the position of molecule when the time is t, and $r_i(0)$ is the initial position. According to Equations (4) and (5), the diffusion coefficients were calculated and are shown in **Table S2 and S3**.

After a series of the diffusion coefficients, D_S, of NO_2 at different temperatures were obtained, the diffusion activation energy of NO_2 could be calculated by means of the Arrhenius equation:

$$D_S = D_0 \exp(-E_a' / RT) \tag{6}$$

where E_a', A, and R refer to the Arrhenius activation energy, the Arrhenius factor, and gas constant, respectively. Equation (6) can also be expressed as:

$$\ln D_S = \ln A - E_a' / RT \tag{7}$$

According to the data in **Table S3** and Equation (7), the diffusion activation energy

E_a' could be directly calculated from the slope of the fitted curve. **Figure 6** shows the Arrhenius temperature dependence of the diffusion coefficients along with the activation energy for diffusion. Therefore, the energy barriers to be overcome in the process of NO_2 diffusion to the monolayer of Ag-C_2N_1 and Cu-C_2N_1 are 2.7 kJ/mol and 2.5 kJ/mol.
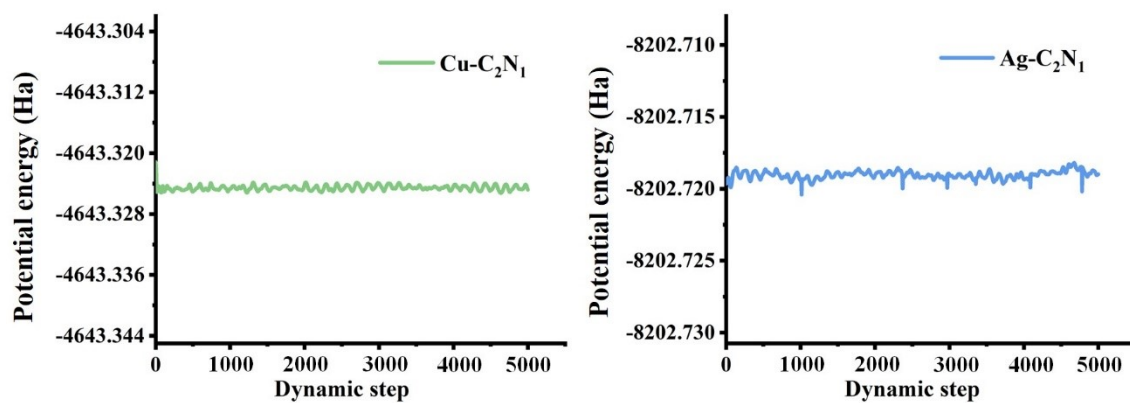
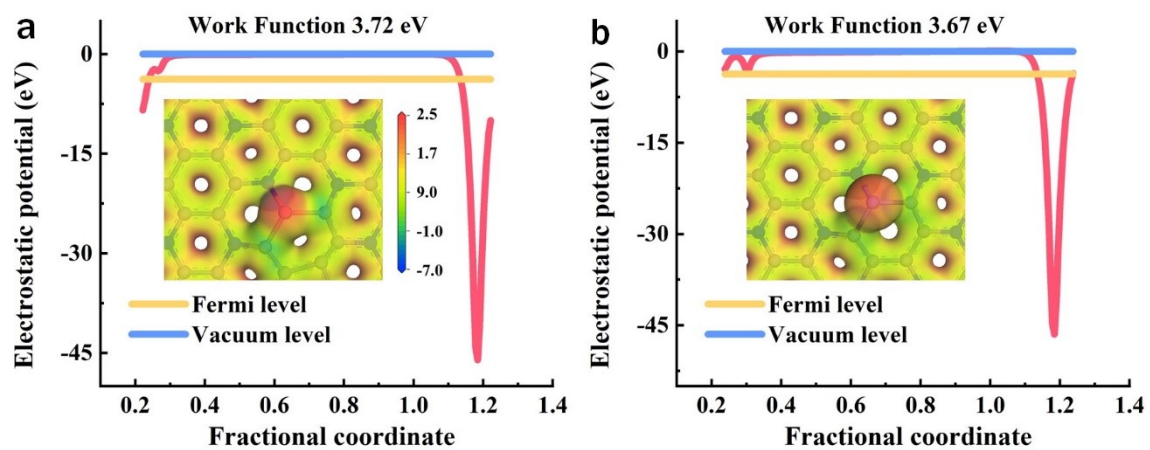**Figure S1.** The energy fluctuations with time process for the *ab initio* molecular dynamics of Cu/Ag-C_2N_1 monolayer.

Figure S2. Electrostatic potential and work function of (a) the Cu-C_2N_1 and (b) the Ag-C_2N_1 monolayer.

Figure S3. Adsorption structures of C_2H_4 at different sites on the Ag-C_2N_1.

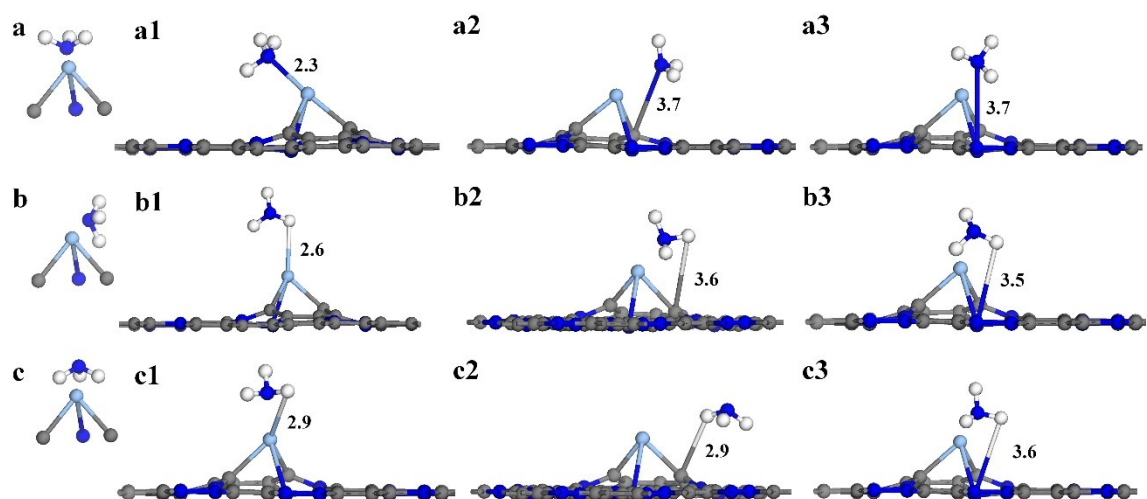**Figure S4.** Adsorption structures of C_2H_6 at different sites on the Ag-C_2N_1.

Figure S5. Adsorption structures of H_2O at different sites on the Ag-C_2N_1.

Figure S6. Adsorption structures of NH_3 at different sites on the Ag-C_2N_1.

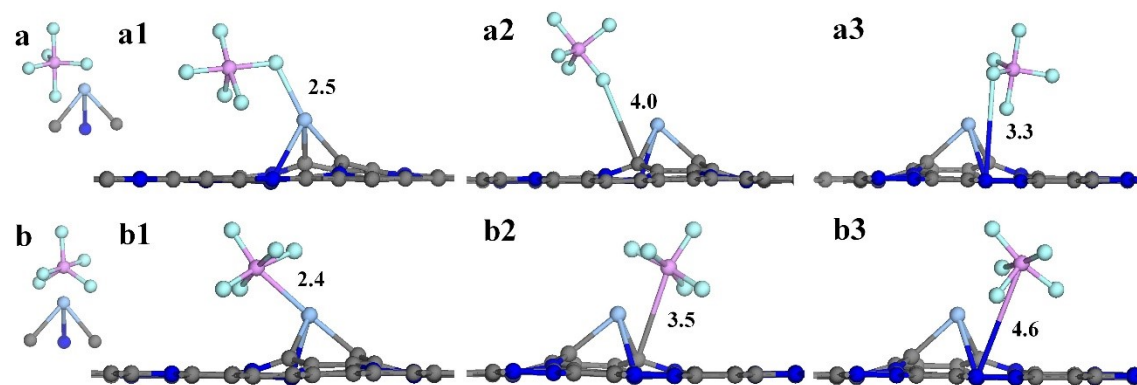**Figure S7.** Adsorption structures of NO$_2$ at different sites on the Ag-C$_2$N$_1$.

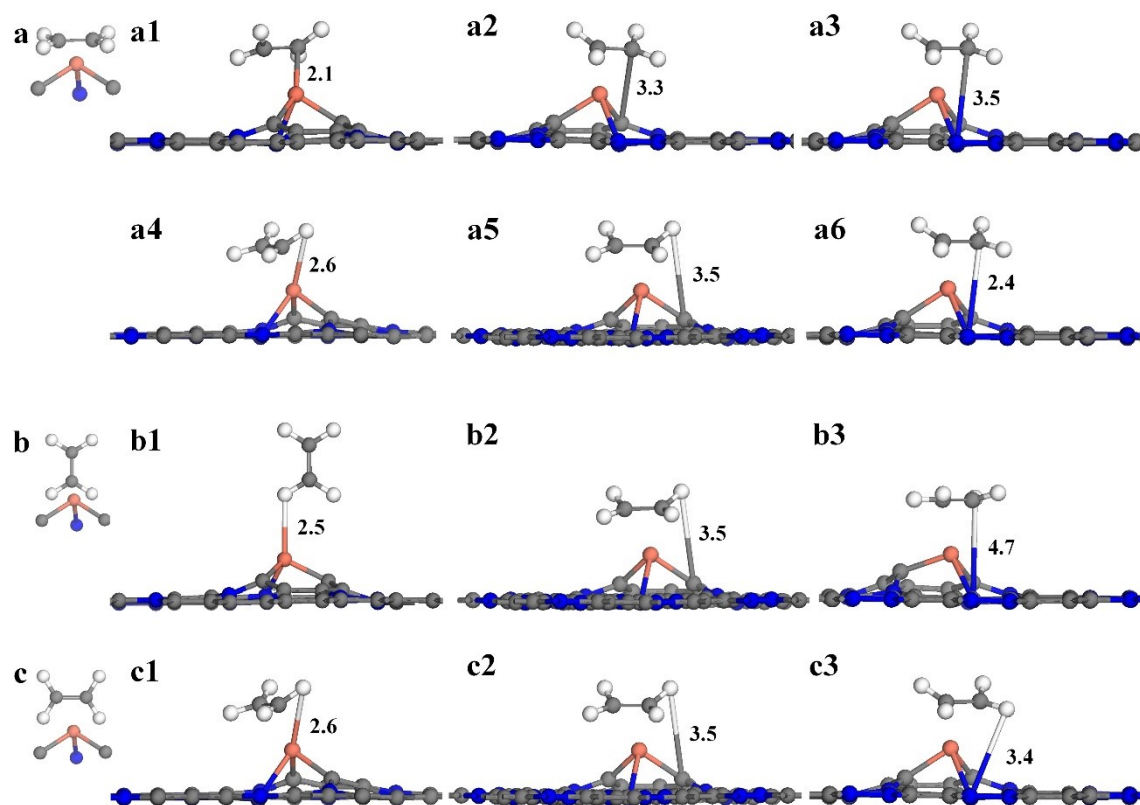**Figure S8.** Adsorption structures of PF_5 at different sites on the Ag-C_2N_1.

Figure S9. Adsorption structures of C_2H_4 at different sites on the Cu-C_2N_1.

a **a1** 2.5 **a2** 3.2 **a3** 3.3
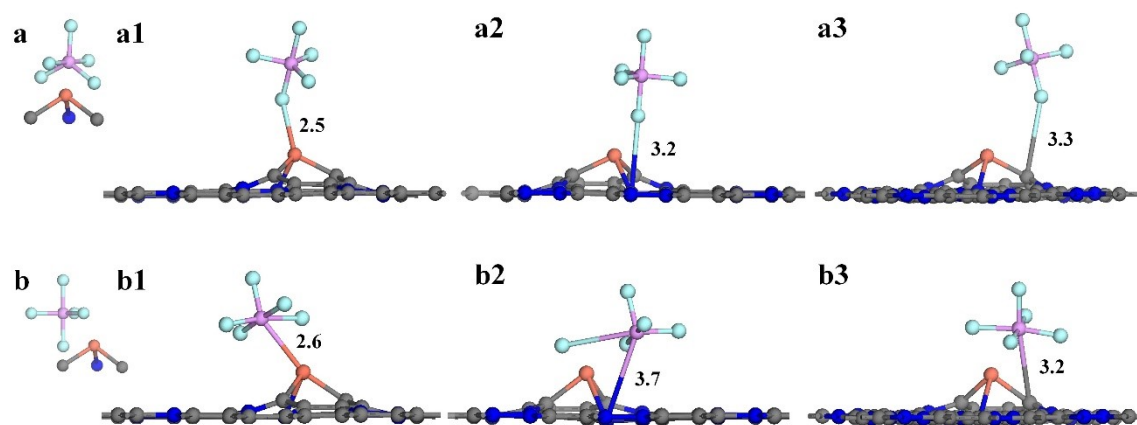
b **b1** 2.6 **b2** 3.7 **b3** 3.2

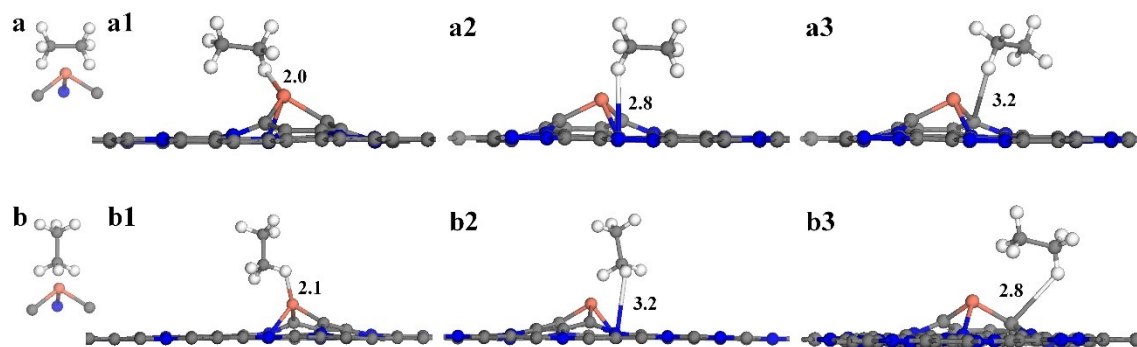**Figure S10.** Adsorption structures of PF_5 at different sites on the $Cu-C_2N_1$.

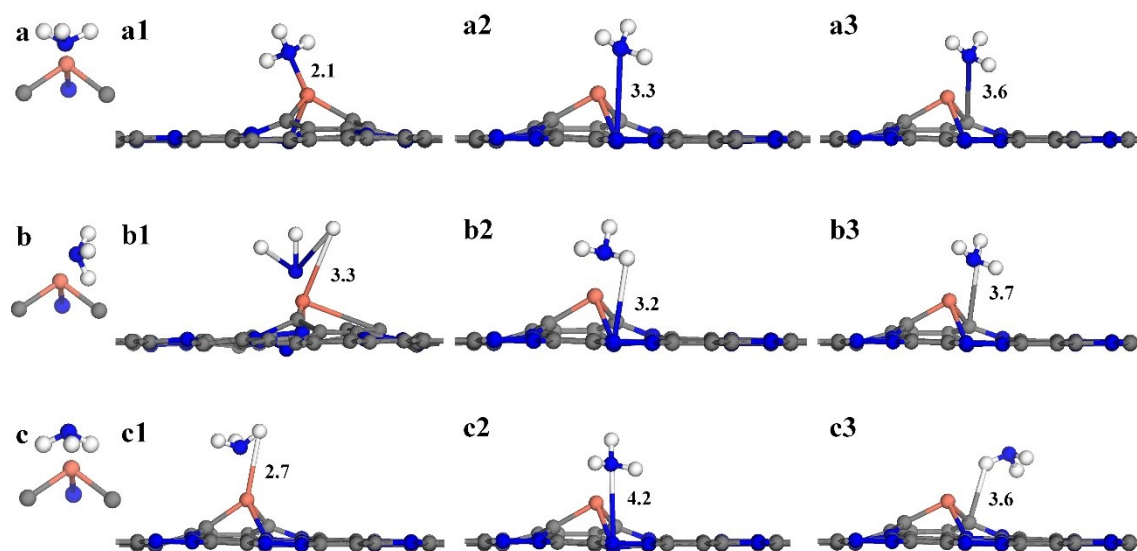**Figure S11.** Adsorption structures of C_2H_6 at different sites on the $Cu-C_2N_1$.

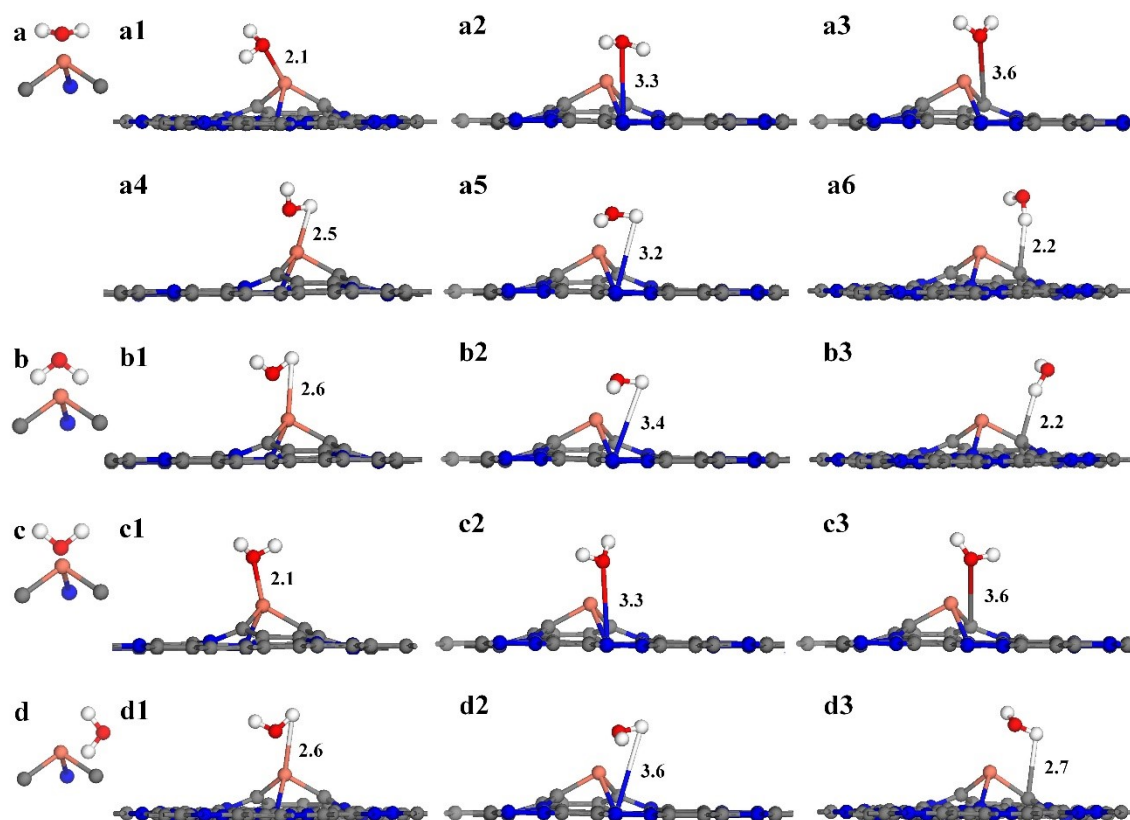**Figure S12.** Adsorption structures of NH_3 at different sites on the $Cu-C_2N_1$.

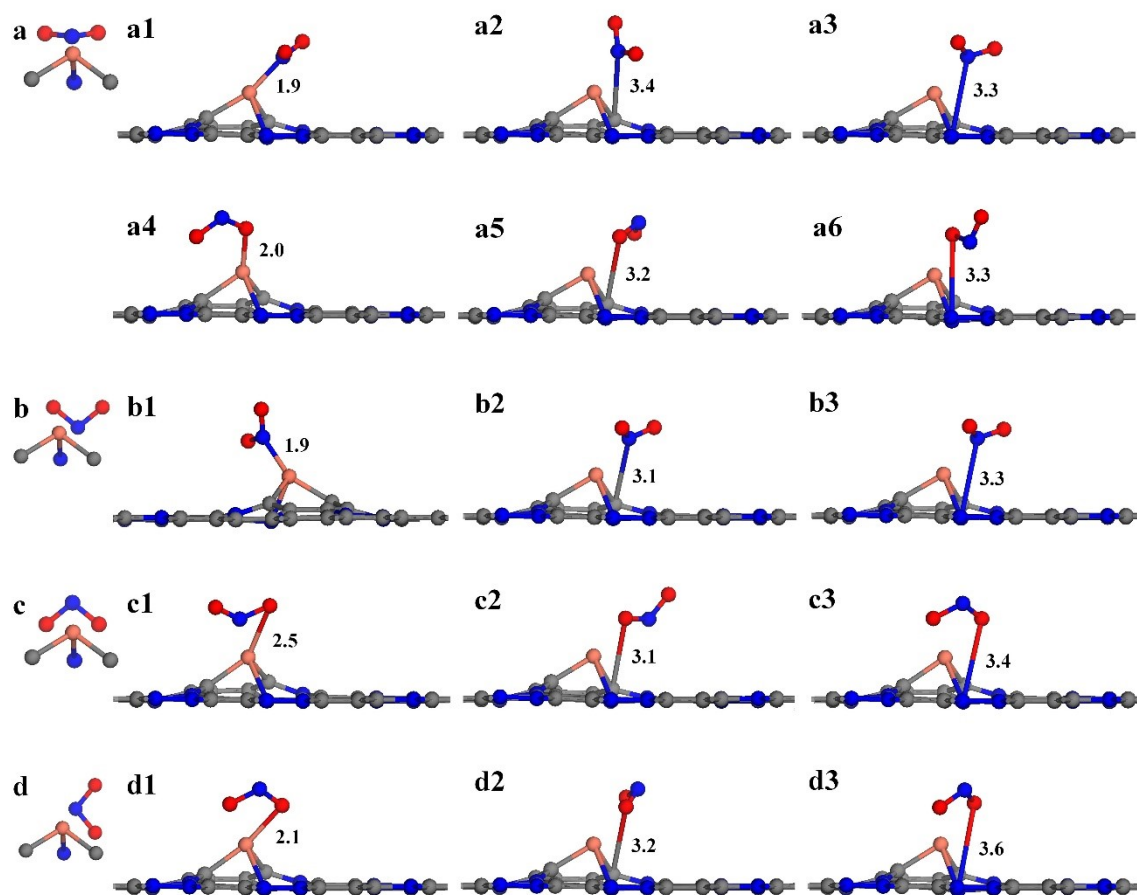**Figure S13.** Adsorption structures of H_2O at different sites on the Cu-C_2N_1.

Figure S14. Adsorption structures of NO_2 at different sites on the Cu-C_2N_1.

Figure S15. The initial adsorption configuration of gases (PF$_5$, NO$_2$, NH$_3$, H$_2$O, C$_2$H$_4$, and C$_2$H$_6$) on the Ag-C$_2$N$_1$.

Figure S16. The initial adsorption configuration of gases (PF_5, NO_2, NH_3, H_2O, C_2H_4, and C_2H_6) on the Cu-C_2N_1.

Figure S17. The COHP between gases (C_2H_4, PF_5, C_2H_6, H_2O, NH_3, and NO_2) and the Ag-C_2N_1.

Figure S18. The COHP between gases (C_2H_4, PF_5, C_2H_6, H_2O, NH_3, and NO_2) and the Cu-C_2N_1.

Figure S19. DOS and PDOS of (a) C_2H_4, (b) C_2H_6, (c) PF_5, (d) H_2O, (e) NH_3, (f) NO_2 on the Ag-C_2N_1 monolayer.

Figure S20. DOS and PDOS of (a) C_2H_4, (b) C_2H_6, (c) PF_5, (d) H_2O, (e) NH_3, (f) NO_2

on the Cu C_2N_1 monolayer.

Figure S21. The initial and the final stable configurations of gas on the Ag-C_2N_1. (a) NH_3, (b) H_2O, (c) PF_5, (d) C_2H_6, (e) C_2H_4, and (f) NO_2.

Figure S22. The initial and the final stable configurations of gas on the Cu-C_2N_1. (a) NH_3, (b) H_2O, (c) PF_5, (d) C_2H_6, (e) C_2H_4, and (f) NO_2.

a

b

c

d

e

Figure S23. The stable configurations of NO_2 on the Ag-C_2N_1 at different temperatures. (a) 300 K, (b) 400 K, (c) 500 K, (d) 600 K, and (e) 700 K.

Figure S24. The stable configurations of NO_2 on the $Cu-C_2N_1$ at different temperatures. (a) 300 K, (b) 400 K, (c) 500 K, (d) 600 K, (e) 700 K, and (f) 800 K.

Table S1. The amount of charge transferred by the gas adsorbed.

Gas	Cu-C_2N_1	Ag-C_2N_1
C_2H_4	-0.09	-0.07
H_2O	0.12	0.09
NO_2	-0.48	-0.44
NH_3	0.16	0.13
C_2H_6	0.10	0.06
PF_5	0.01	-0.91

Table S2. Diffusion coefficient of six gases on the Cu/Ag-C_2N_1 monolayer at 300 K.

Gas	Cu-C_2N_1	Ag-C_2N_1
C_2H_4	4.89	5.78
H_2O	6.73	6.60
NO_2	2.47	2.83
NH_3	5.37	5.07
C_2H_6	4.89	4.13
PF_5	4.39	3.72

Table S3. Diffusion coefficients of NO_2 on the Cu/Ag-C_2N_1 at different temperatures.

T (K)	300	400	500	600	700	800
Cu-C_2N_1	2.47	3.12	3.37	4.44	4.03	4.24
Ag-C_2N_1	2.83	3.47	3.78	3.70	5.18	-

Table S4. The recovery time (s) of the gas on the Cu-C_2N_1.

T(K)	C_2H_4	H_2O	NO_2	NH_3	C_2H_6	PF_5
273	4.3×10^{24}	2.0×10^3	1.9×10^{53}	6.9×10^{13}	11.6	3.6×10^{-9}
300	2.2×10^{21}	83.6	2.5×10^{47}	3.2×10^{11}	0.8	1.7×10^{-9}
400	1.0×10^{13}	2.0×10^{-2}	3.6×10^{32}	4.3×10^5	8.3×10^{-4}	2.7×10^{-10}
500	1.0×10^8	2.3×10^{-4}	4.4×10^{23}	1.3×10^2	1.4×10^{-5}	8.8×10^{-11}
600	4.7×10^4	9.1×10^{-6}	5.0×10^{17}	0.6	8.8×10^{-7}	4.2×10^{-11}
700	1.9×10^2	9.3×10^{-7}	2.9×10^{13}	1.2×10^{-2}	1.2×10^{-7}	2.4×10^{-11}
800	3.2	1.7×10^{-7}	1.9×10^{10}	6.6×10^{-4}	2.9×10^{-8}	1.6×10^{-11}

Table S5. The recovery time (s) of the gas on the Ag-C_2N_1.

T(K)	C_2H_4	H_2O	NO_2	NH_3	C_2H_6	PF_5
273	4.8×10^{16}	49.4	1.9×10^{48}	1.4×10^{10}	5.8×10^{-4}	4.4×10^5
300	1.3×10^{14}	2.9	7.1×10^{42}	1.4×10^8	9.5×10^{-5}	1.1×10^4
400	3.7×10^7	2.2×10^{-3}	1.4×10^{29}	1.3×10^3	9.6×10^{-7}	1.1
500	4.6×10^3	3.0×10^{-5}	8.1×10^{20}	1.2	6.1×10^{-8}	4.3×10^{-3}
600	11.2	1.7×10^{-6}	2.7×10^{15}	1.2×10^{-2}	9.7×10^{-9}	1.1×10^{-4}
700	0.2	2.2×10^{-7}	3.2×10^{11}	4.3×10^{-4}	2.6×10^{-9}	7.6×10^{-6}

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