

## PAPER

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The pressing need for affordable gas sensors with enhanced sensitivity and selectivity in identifying hazardous gases released after the battery becomes unstable cannot be overstated. In this study, a C<sub>3</sub>N<sub>1</sub> monolayer modified with Cu and Ag atoms (Cu/Ag–C<sub>2</sub>N<sub>1</sub>) was selected to achieve selective adsorption of NO<sub>2</sub> under the coexistence of multiple gases (PF<sub>5</sub>, NH<sub>3</sub>, H<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>) based on density functional theory. The results demonstrate that securely anchoring metal atoms to the monolayer, as indicated by cohesion energy and *ab initio* molecular dynamics simulations, concurrently enhances the material's conductivity. Analyses of electrostatic potential and work function identified high activity sites and electron-releasing capabilities. Furthermore, the gas–solid interface structures of multiple gases on the Cu/Ag–C<sub>2</sub>N<sub>1</sub> monolayers are revealed by the adsorption energy and distance. Importantly, NO<sub>2</sub> exhibits stronger adsorption energy on Cu/Ag–C<sub>2</sub>N<sub>1</sub>, reaching –3.54 and –3.27 eV, respectively. Crystal Orbital Hamilton Population and d-band center theory unveiled differences in adsorption energy resulting from the modification involving the two metals. Fascinatingly, density of states calculation demonstrates, for the first time, that the two doped metal monolayers generate a distinct response solely to NO<sub>2</sub> in a multi-gas coexistence setting, effectively excluding interference from water. In practice, based on Gibbs free energy and Einstein diffusion law calculations, Cu–C<sub>2</sub>N<sub>1</sub> exhibits superior hydrophobicity, a broader temperature range and a lower diffusion activation energy barrier (2.5 kJ mol<sup>–1</sup>). Our theoretical calculations demonstrate Cu's efficacy in substituting expensive Ag, yielding cost-effectiveness without compromising selectivity, response, stability, and versatility.

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## 1 Introduction

Widespread in portable electronics and integral to the surge in electric vehicles, batteries play a pivotal role, significantly impacting the tapestry of modern society.<sup>1–3</sup> However, the pursuit of high-energy-density batteries raises safety concerns due to increased gas evolution, particularly with lithium metal.<sup>4,5</sup> Safety monitoring is vital as battery defects can trigger severe risks like electrolyte-induced heat leading to fire and explosion. This thermal runaway results in the release of harmful gases.<sup>6</sup> Lithium metal poses challenges due to its reactivity, potentially causing dendritic formation and a hot mixture release, a precursor to fire or explosion. Early detection

of gases like NO<sub>2</sub>, PF<sub>5</sub>, NH<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>O, and C<sub>2</sub>H<sub>6</sub> before thermal runaway is imperative to prevent safety hazards in practical applications.<sup>7,8</sup>

In recent years, an abundance of theoretical studies has delved into the design and fabrication of monolayers for detecting toxic gases. Theoretical calculations, employing density functional theory (DFT), have played a pivotal role in accurately predicting the sensing efficiency of two-dimensional (2D) monolayers and elucidating their micro-sensing mechanisms.<sup>9–17</sup> For instance, Sun *et al.*<sup>18</sup> utilized DFT calculations to analyze the adsorption behavior of six gases on an indium nitride monolayer, demonstrating its potential in detecting SO<sub>2</sub> and NO<sub>2</sub> molecules. Additionally, first-principles calculations were employed to explore the structural and electronic properties of group III nitrides and phosphides in gas adsorption. It was concluded that significant potential exists for the detection of CO<sub>2</sub> by these sensors. Furthermore, the introduction of transition metal doping can enhance the sensing capabilities of 2D monolayers.<sup>19–21</sup>

In gas-sensitive applications, 2D monolayers demonstrate exceptional performance owing to their high specific monolayer area, thermal conductivity, unique optoelectronic properties, and catalytic activity.<sup>22–25</sup> As chemical gas sensors, these

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monolayer offer abundance, cost-effectiveness, and easy manufacturability, and play a pivotal role in sensor technology. Among numerous 2D material-based gas sensors, their sensitivity to various toxic and explosive gases stems from gas-induced resistance changes,<sup>26</sup> finding wide application across diverse fields. Graphene and C<sub>3</sub>N monolayer films, among others, have theoretically shown promising gas-sensing characteristics.<sup>27–29</sup> Despite this, inherent defects limit the full application potential of 2D monolayers in sensing technologies. Hence, exploring and discovering novel types of two-dimensional monolayers for gas detection become imperative to address these limitations and expand the sensor monolayer repertoire.

Creating new gas sensors to detect typical electrolyte decomposition products under harsh conditions is crucial. 2D monolayers stand out as prime candidates for such sensing applications, operating within a high temperature range and exhibiting the highest response levels.<sup>30</sup> Enhancing gas sensor characteristics involves monolayer material modification. Semiconductor-based metal oxide gas sensors also require temperature resistance during thermal runaway, making safety-based detectors particularly promising. These devices offer stability under high humidity conditions but demand high-temperature resilience during thermal runaway.<sup>31,32</sup> Metal-doped 2D material gas sensors exhibit notably high responses, showcasing how metals create a platform to merge diverse physical and chemical properties within a system. Past research has amalgamated experiments and intricate computational analyses to validate the applicability of metal-doped structures in sensor applications.<sup>33–36</sup> These studies have visualized the gas sensing traits, portraying the adsorption performance of gas sensors for practical implementation.

However, the electrical response of the sensing monolayer originates from the cumulative effect of each gas. The significant scientific challenge lies in the absence of an effective method to systematically allocate the contribution of each gas. Consequently, in the case of the simultaneous adsorption of multiple gases, the strategy to enhance selectivity involves eliminating the electrical response to other interfering gases, focusing solely on one specific gas.

In this study, DFT was employed to calculate the response of Cu/Ag–C<sub>2</sub>N<sub>1</sub> in the presence of multiple gases (PF<sub>5</sub>, NO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>). Initially, 2D monolayers doped with these two metals were constructed, and their stability and plausibility were examined from various perspectives. Subsequently, the adsorption behavior of multiple gases on the doped monolayer was comprehensively calculated, elucidating differences in adsorption performance based on methods such as d-band center theory and Crystal Orbital Hamiltonian Population (COHP). Utilizing the density of states (DOS) method, the electrical signal response behavior of the monolayer during the adsorption of multiple gases for selective adsorption was evaluated. Finally, the practical applicability of the sensors was explored by computing the Gibbs free energy of gas adsorption and the recovery time of the electrical signal. Our theoretical exploration offers novel insights for designing highly selective gas sensors in battery instability monitoring.

## 2 Results and discussion

### 2.1 Structural characterization

The optimized structures of the Cu/Ag–C<sub>2</sub>N<sub>1</sub> monolayer and six gas molecules (PF<sub>5</sub>, NO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>) are shown in Fig. 1a. It exhibits a top-down view of the metal-modified C<sub>2</sub>N<sub>1</sub> monolayer, comprising a pattern of corner rings formed by C–N–C–C sequences, while also illustrating the interaction sites of Ag and Cu. In detail, the P–F bond length in PF<sub>5</sub> is 1.58 Å, the N–O bond length in NO<sub>2</sub> is 1.27 Å, the N–H bond length in NH<sub>3</sub> is 1.03 Å, and the H–O bond length in H<sub>2</sub>O is 0.98 Å. For C<sub>2</sub>H<sub>4</sub>, the C–H bond length is 1.09 Å, and the C–C bond length is 1.33 Å. For C<sub>2</sub>H<sub>6</sub>, the C–H bond length is 1.06 Å, and the C–C bond length is 1.53 Å. These data calculated in this work are consistent with those previously reported,<sup>37–44</sup> demonstrating that the selected calculation parameters are reasonable and accurate. Fig. 1b and c depict the main view of the monolayer of Ag–C<sub>2</sub>N<sub>1</sub> and Cu–C<sub>2</sub>N<sub>1</sub>, respectively. Clearly, both doped metals are situated atop the 2D material, creating the most stable structure, in accordance with earlier research observations.<sup>28</sup> So as to understand the monolayer stability of doped metal atoms from the point of view of charge density, Fig. 1b and c also illustrate distinct charge density distribution. The noticeable increase in red indicates a heightened charge density of electronic wavefunction, predominantly around the C and N atoms, confirming its high charge acceptance. Both Ag and Cu act as electron donors, transferring electrons to C<sub>2</sub>N<sub>1</sub>. Therefore, to maintain an optimal stable structure, the doped metal atoms ultimately position themselves above the monolayer, resulting in substrate deformation.

Additionally, cohesion energy ( $E_{\text{coh}}$ ) analyses were conducted to quantitatively explore the anchoring of metal atoms onto the monolayer. First, the  $E_{\text{coh}}$  was analyzed as:<sup>45</sup>

$$E_{\text{coh}} = \frac{(n_1 E_{\text{TM}} + n_2 E_{\text{C}} + n_3 E_{\text{N}} - E_{\text{C}_2\text{N}_1})}{(n_1 + n_2 + n_3)} \quad (1)$$

where  $E_{\text{C}}$  and  $E_{\text{N}}$  represent the energies (eV) of C and N atoms, respectively.  $n_1$ ,  $n_2$ , and  $n_3$  are the numbers of metal, C, and N atoms. The  $E_{\text{coh}}$  of the initial C<sub>3</sub>N<sub>1</sub> monolayer was calculated to be 7.01 eV. After metal doping, it decreased to 6.67 eV for Cu–C<sub>2</sub>N<sub>1</sub> and 6.70 eV for Ag–C<sub>2</sub>N<sub>1</sub>, showcasing a reduction within the expected range of 4%. This highlights the stable bonding of metals to the monolayer without undergoing aggregation. To evaluate the dynamic stability of this structure, *ab initio* molecular dynamics simulation was conducted. A total of 5000 steps were calculated over 50 ps, using a time step of 10 fs for output. The results, confirming the stability of the monolayer structures, are illustrated in Fig. S1.† In the realm of top-notch gas sensors, it's crucial to understand the electron transport capabilities and active sites of the material for optimal performance. The electrostatic potential and work function were calculated, with the work function representing the minimum energy required to remove electrons from the monolayer. As shown in Fig. S2,† the results reveal a comparable work function for Ag–C<sub>2</sub>N<sub>1</sub> (3.67 eV) and Cu–C<sub>2</sub>N<sub>1</sub> (3.72 eV), suggesting a similar electron migration capability. Furthermore, based on

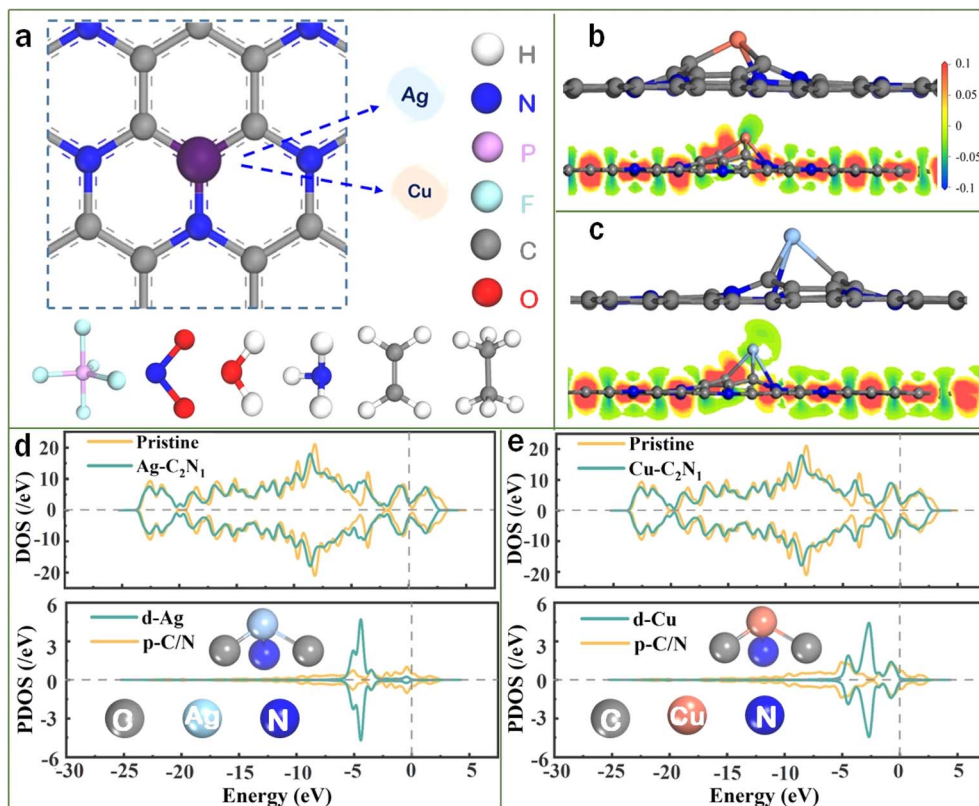


Fig. 1 (a) Structures of the Cu/Ag- $C_2N_1$  monolayer,  $PF_5$ ,  $NO_2$ ,  $NH_3$ ,  $H_2O$ ,  $C_2H_4$ , and  $C_2H_6$ . (b and c) Stable structure and charge density distribution of (b) Cu- $C_2N_1$  and (c) Ag- $C_2N_1$ . (d and e) DOS and PDOS of (d) Ag- $C_2N_1$  and (e) Cu- $C_2N_1$ . Densities are displayed with an isosurface and the interval of isovalues is between  $-0.1$  and  $0.1 \text{ e } \text{\AA}^{-3}$ .

the high electrostatic potential, it can be confirmed that the doped metal sites exhibit heightened activity.

Based on previous research,<sup>12,19,46–49</sup> the height of the DOS curve at the Fermi level can reflect the quality of material conductivity. In other words, higher peaks indicate better conductivity. Conductivity stands as a crucial criterion for high-performance gas sensors. Therefore, this study employs this approach to assess the impact of introducing doping metals on the material's conductivity. In Fig. 1d and e, the overall DOS demonstrates a slight increase in the curve around the Fermi level after the introduction of doping metals, indicating an enhancement in the material's conductivity. Additionally, partial density of states (PDOS) calculations were conducted to delve deeper into the behavior of the doped metal atoms. Fig. 1d and e display the d orbitals of the metal atoms and the p-orbitals of nonmetallic C/N in the monolayer. Typically, transition metal d-orbitals play a significant role in bonding. The outcomes reveal a noticeable alignment between the d orbital of Ag and the p orbital of C/N within the material. Furthermore, the hybridization of Cu's d orbital with C/N's p orbital is more prominent and situated at a higher energy level. The findings indicate that Cu and Ag can be securely affixed to the  $C_2N_1$  monolayer. This indicates a robust interaction between the doped metal atoms and the monolayers, ensuring structural stability.

## 2.2 Gas sensing performance

**2.2.1 Gas adsorption behavior.** In this section, the optimal gas adsorption configurations were initially identified. Subsequently, the adsorption energy and distance were quantitatively analyzed. Finally, the differences in gas adsorption performance were elucidated using COHP and d-band center theory. As depicted in Fig. S3–S14,<sup>†</sup> various gas adsorption sites and configurations were explored on Ag- $C_2N_1$  and Cu- $C_2N_1$ . Initially, all gas molecules positioned  $2.5 \text{ \AA}$  above the monolayer underwent structural optimization calculations to determine their equilibrium positions. Based on the positive correlation between the adsorption distance and energy,<sup>50,51</sup> the initial configurations following this criterion were selected, as illustrated in Fig. S15 and S16.<sup>†</sup> Fig. 2 and 3 show the most stable adsorption configurations and charge densities of Ag- $C_2N_1$  and Cu- $C_2N_1$  for the six gases ( $C_2H_4$ ,  $PF_5$ ,  $C_2H_6$ ,  $H_2O$ ,  $NH_3$ , and  $NO_2$ ).

In Fig. 2, the shortest atomic distances observed are  $2.3 \text{ \AA}$  for Ag- $C_2N_1$ - $C_2H_4$ ,  $2.5 \text{ \AA}$  for Ag- $C_2N_1$ - $PF_5$ ,  $2.2 \text{ \AA}$  for Ag- $C_2N_1$ - $C_2H_6$ ,  $2.5 \text{ \AA}$  for Ag- $C_2N_1$ - $H_2O$ ,  $2.3 \text{ \AA}$  for Ag- $C_2N_1$ - $NH_3$ , and  $2.2 \text{ \AA}$  for Ag- $C_2N_1$ - $NO_2$ . In Fig. 3, the shortest atomic distances are  $2.1 \text{ \AA}$  for Cu- $C_2N_1$ - $C_2H_4$ ,  $2.5 \text{ \AA}$  for Cu- $C_2N_1$ - $PF_5$ ,  $2.0 \text{ \AA}$  for Cu- $C_2N_1$ - $C_2H_6$ ,  $2.1 \text{ \AA}$  for Cu- $C_2N_1$ - $H_2O$ ,  $2.1 \text{ \AA}$  for Cu- $C_2N_1$ - $NH_3$ , and  $1.9 \text{ \AA}$  for Cu- $C_2N_1$ - $NO_2$ . After optimization, the positions of all gas molecules have shifted. The shortest distance of each gas molecule in the Ag- $C_2N_1$  system is slightly longer than that of

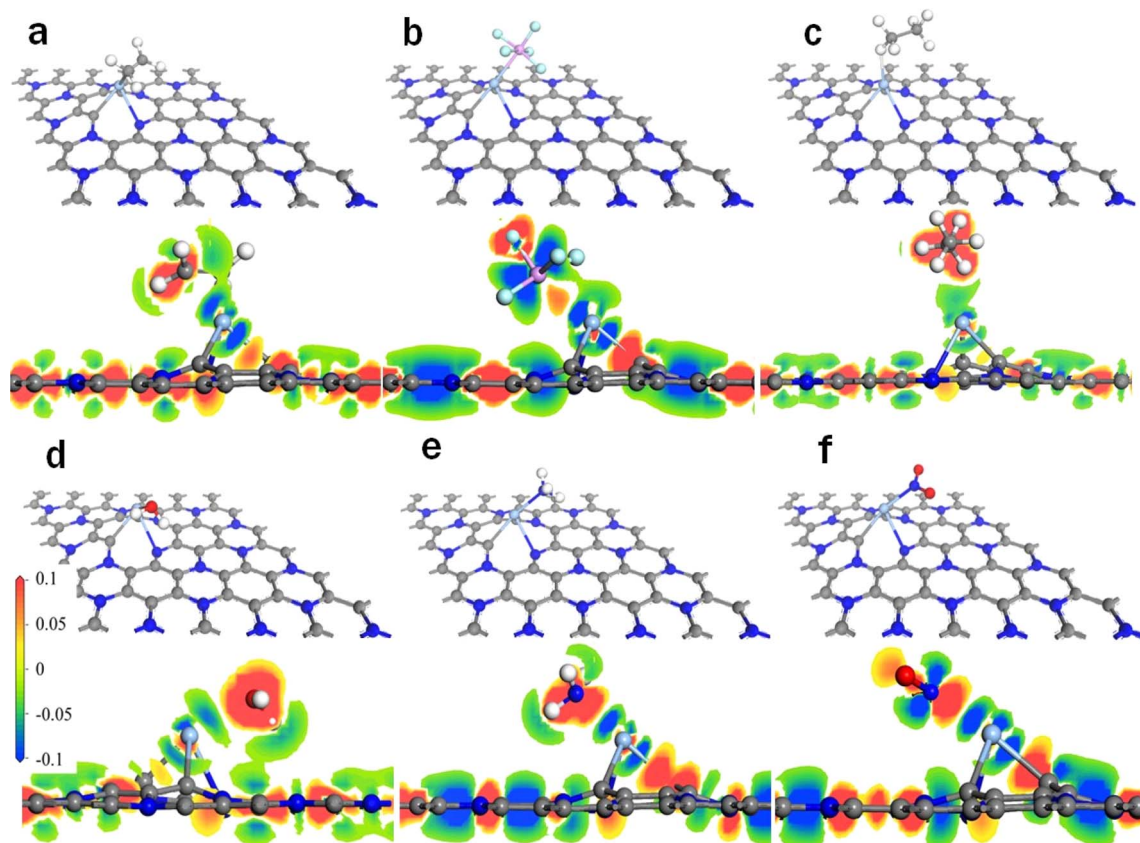


Fig. 2 Stable configurations and charge density of gas adsorbed on the Ag-C<sub>2</sub>N<sub>1</sub> monolayer: (a) Ag-C<sub>2</sub>N<sub>1</sub>-C<sub>2</sub>H<sub>4</sub>, (b) Ag-C<sub>2</sub>N<sub>1</sub>-C<sub>2</sub>H<sub>6</sub>, (c) Ag-C<sub>2</sub>N<sub>1</sub>-PF<sub>5</sub>, (d) Ag-C<sub>2</sub>N<sub>1</sub>-H<sub>2</sub>O, (e) Ag-C<sub>2</sub>N<sub>1</sub>-NH<sub>3</sub>, and (f) Ag-C<sub>2</sub>N<sub>1</sub>-NO<sub>2</sub>. Densities are displayed with an isosurface and the interval of isovalues is between -0.1 and 0.1 e Å<sup>-3</sup>.

the Cu-C<sub>2</sub>N<sub>1</sub> system. Additionally, for a more visual examination of the charge accumulation and depletion during gas interaction with Cu/Ag-C<sub>2</sub>N<sub>1</sub>, Fig. 2 and 3 present the results of charge density analysis. The charge densities of electronic wavefunction illustrate that both Ag-C<sub>2</sub>N<sub>1</sub> and Cu-C<sub>2</sub>N<sub>1</sub> transfer a significant amount of charge during gas adsorption. The distinct dark red color observed around the gas molecules (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, PF<sub>5</sub>, H<sub>2</sub>O, NH<sub>3</sub>, and NO<sub>2</sub>) clearly indicates the acquisition of electrons from Ag-C<sub>2</sub>N<sub>1</sub> and Cu-C<sub>2</sub>N<sub>1</sub> by the gas molecules, demonstrating a strong interaction between the gas and Cu/Ag-C<sub>2</sub>N<sub>1</sub>. For specific charge transfer values, refer to Table S1.† The results indicate that among the six gases considered, NO<sub>2</sub> exhibited the most significant charge transfer to Cu/Ag-C<sub>2</sub>N<sub>1</sub>, suggesting its superior adsorption effect on it, particularly on the Cu-C<sub>2</sub>N<sub>1</sub> monolayer.

For a more comprehensive understanding of gas adsorption behavior and to quantitatively assess the interaction forces between gases and Cu/Ag-C<sub>2</sub>N<sub>1</sub>, it becomes imperative to compare adsorption distances and energies. Fig. 4a and b show respectively the adsorption distance and adsorption energy. The adsorption energy is defined as:<sup>52–54</sup>

$$E_{\text{ads}} = E_{\text{total}} - (E_{\text{monolayer}} + E_{\text{gas}}) \quad (2)$$

where  $E_{\text{ads}}$  is the adsorption energy (eV),  $E_{\text{total}}$  is the total energy of the monolayer with the gas molecule (eV),  $E_{\text{monolayer}}$  is the total energy of the monolayer (eV), and  $E_{\text{gas}}$  is the total energy of an isolated gas molecule (eV). For the adsorption distance, the darker the color, the shorter the adsorption distance. From Fig. 4a it can be intuitively seen that the color of the row where Cu is located is darker than the color of the row where Ag is located, that is, the adsorption distance of the gas under the Cu system is less than that of the Ag system, indicating that the Cu-C<sub>2</sub>N<sub>1</sub> monolayer has better adsorption performance for the gas. The adsorption distance of Cu-C<sub>2</sub>N<sub>1</sub>-NO<sub>2</sub> is the smallest, showcasing the exceptional adsorption effectiveness of Cu-C<sub>2</sub>N<sub>1</sub> for NO<sub>2</sub>. Additionally, Cu-C<sub>2</sub>N<sub>1</sub> exhibits relatively small adsorption distances for C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, NH<sub>3</sub>, and H<sub>2</sub>O, indicating noteworthy adsorption performance. However, the analysis of adsorption energy suggests that Cu-C<sub>2</sub>N<sub>1</sub> interacts with C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and NH<sub>3</sub> through physical adsorption based on our previous work.<sup>19</sup> The column where NO<sub>2</sub> is situated appears significantly darker compared to the columns of the other gases (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, NH<sub>3</sub>, H<sub>2</sub>O, and PF<sub>5</sub>) in Fig. 4b. This implies that among the six gases, only NO<sub>2</sub> exhibits a pronounced adsorption effect on the C<sub>2</sub>N<sub>1</sub> monolayer after metal doping, and its adsorption energy is much stronger than that of the other five gases. This realization enables the selective adsorption of NO<sub>2</sub> gas on the monolayer in various gas environments, unaffected

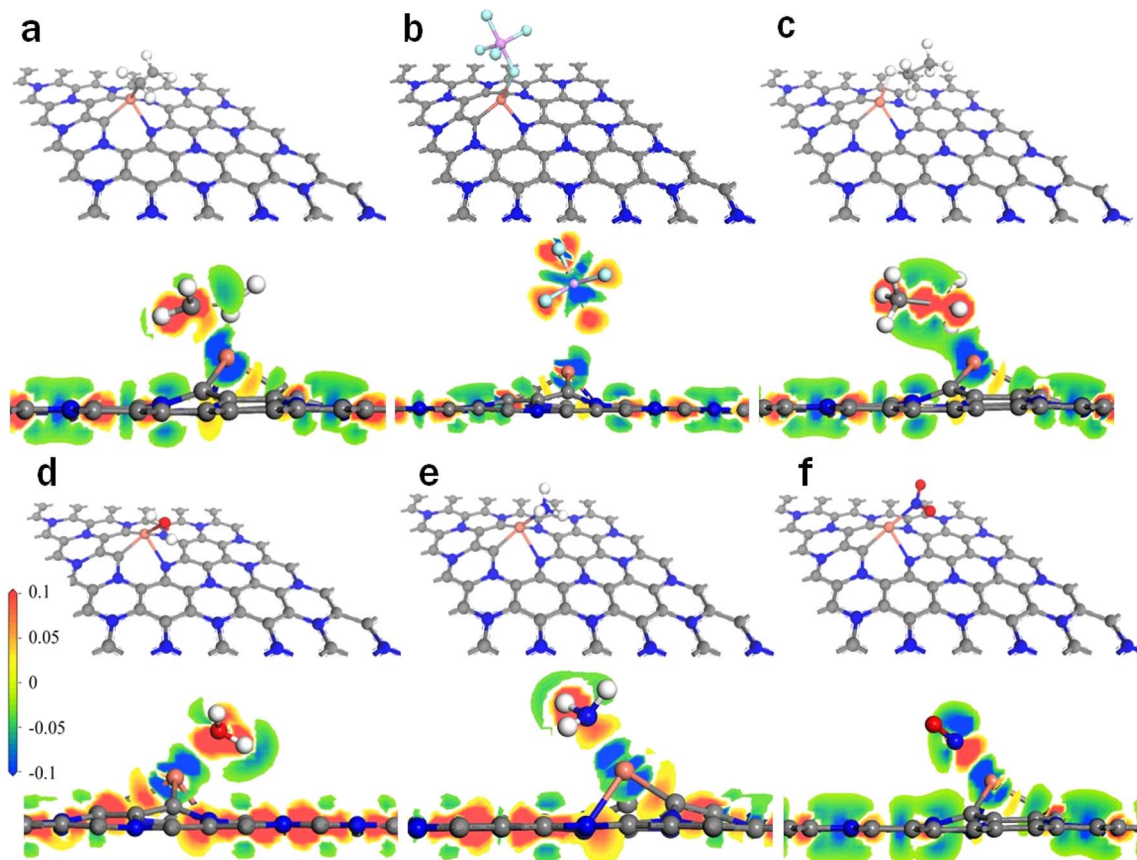


Fig. 3 Stable configurations and charge density of gas adsorbed on the Cu-C<sub>2</sub>N<sub>1</sub> monolayer: (a) Cu-C<sub>2</sub>N<sub>1</sub>-C<sub>2</sub>H<sub>4</sub>, (b) Cu-C<sub>2</sub>N<sub>1</sub>-C<sub>2</sub>H<sub>6</sub>, (c) Cu-C<sub>2</sub>N<sub>1</sub>-PF<sub>5</sub>, (d) Cu-C<sub>2</sub>N<sub>1</sub>-H<sub>2</sub>O, (e) Cu-C<sub>2</sub>N<sub>1</sub>-NH<sub>3</sub>, and (f) Cu-C<sub>2</sub>N<sub>1</sub>-NO<sub>2</sub>.

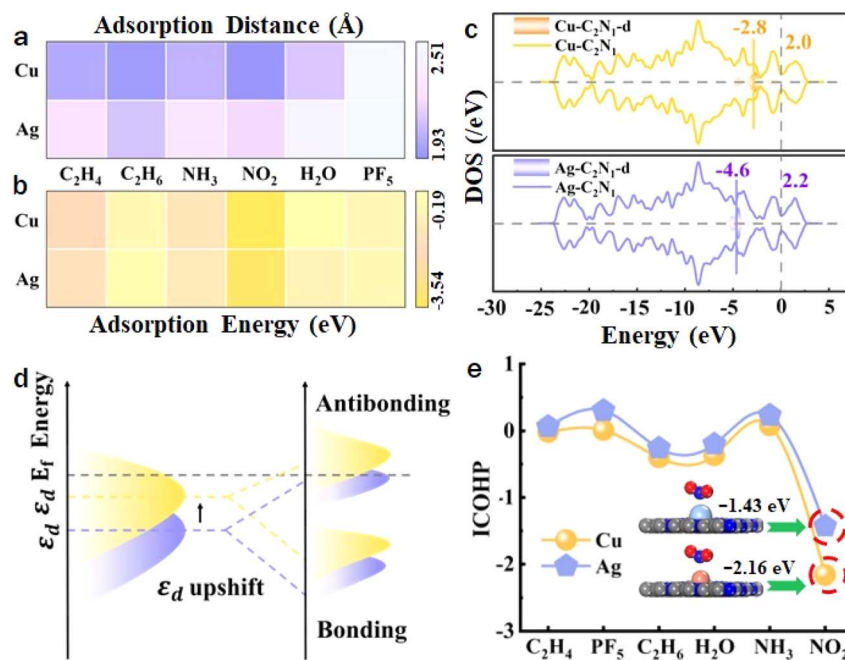


Fig. 4 (a) The adsorption distance and (b) adsorption energy of gases (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, NH<sub>3</sub>, NO<sub>2</sub>, H<sub>2</sub>O, and PF<sub>5</sub>) on the Ag-C<sub>2</sub>N<sub>1</sub> and Cu-C<sub>2</sub>N<sub>1</sub> monolayers. (c) The d-band center of C<sub>2</sub>N<sub>1</sub> doped with metals (Cu and Ag). (d) Metal-adsorbate interaction by altering the metal d-band center. (e) ICOHP of gases on the Ag-C<sub>2</sub>N<sub>1</sub> and Cu-C<sub>2</sub>N<sub>1</sub> monolayers.

by the presence of other gases. Additionally, it's noteworthy that the adsorption energy of H<sub>2</sub>O on Cu-C<sub>2</sub>N<sub>1</sub> is weaker, indicating that Cu-C<sub>2</sub>N<sub>1</sub> exhibits virtually no adsorption effect on H<sub>2</sub>O. Consequently, humid environments do not affect the performance of Cu-C<sub>2</sub>N<sub>1</sub>.

Combining the different gas adsorption properties caused by the above two doped metal atoms, it can be found that the performance of Cu is better than that of Ag. For example, the adsorption energy of Cu-C<sub>2</sub>N<sub>1</sub>-NO<sub>2</sub> is -3.53 eV, which is stronger than that of Ag-C<sub>2</sub>N<sub>1</sub>-NO<sub>2</sub> (-3.26 eV). Given that d-band center theory is a useful tool for elucidating the interaction between transition metals and gas molecules, the calculation of the d-band center ( $\varepsilon_d$ ) becomes imperative to unveil the underlying mechanism. The  $\varepsilon_d$  can be calculated as:<sup>55–57</sup>

$$\varepsilon_b = \frac{\int_{-\infty}^{\infty} n_d(\varepsilon) \varepsilon d\varepsilon}{\int_{-\infty}^{\infty} n_d(\varepsilon) d\varepsilon} \quad (3)$$

where  $\varepsilon$  is the energy and  $n_d(\varepsilon)$  is the density. Fig. 4c shows the  $\varepsilon_d$  of Cu/Ag-C<sub>2</sub>N<sub>1</sub>. The larger the  $\varepsilon_d$  (close to the Fermi level), the better the adsorption effect on gas. It is better proved that NO<sub>2</sub> has the greatest adsorption strength on Cu-C<sub>2</sub>N<sub>1</sub>. Fig. 4d shows that the  $\varepsilon_d$  of Cu-C<sub>2</sub>N<sub>1</sub> is closest to the Fermi level, demonstrating that the proportion of unoccupied antibonding states increases, resulting in the strongest interaction between NO<sub>2</sub> and Cu-C<sub>2</sub>N<sub>1</sub>.

To expose disparities in gas adsorption energy on Cu-C<sub>2</sub>N<sub>1</sub> and Ag-C<sub>2</sub>N<sub>1</sub> from a chemical bonding perspective, the chemical bond is categorized into bonding and anti-bonding, with bonding playing the decisive role. COHP analysis is employed for a more accurate examination of interatomic forces during gas adsorption.<sup>58–61</sup> The detailed calculation results are displayed in Fig. S17 and S18.† COHP represents the respective contributions of bonding and antibonding and shows the strength of the chemical bond between atoms, and the larger the bonding state below the Fermi level, the smaller the anti-bonding state, the stronger the bonding ability between the two atoms. In the example Fig. S17† of Ag-C<sub>2</sub>N<sub>1</sub>-PF<sub>5</sub>, there are a large number of anti-bonds below the Fermi level, resulting in a huge internal stress between Ag and F atoms, and the anti-bonds in the system cause repulsion between the atoms, and the interaction cannot be stable. In contrast, there is a large amount of bonding below the Fermi level in Cu-C<sub>2</sub>N<sub>1</sub>-NO<sub>2</sub> in Fig. S18,† indicating that there is a strong force between Cu and N, which confirms the strong interaction between Cu-C<sub>2</sub>N<sub>1</sub> and NO<sub>2</sub>. A more quantitative explanation can be provided by calculating the integral COHP (ICOHP) value obtained by calculating the energy integral from negative infinity to the Fermi level. The more negative the ICOHP value, the stronger the interaction between metal atoms and gas atoms, as shown in Fig. 4e. Compared to the other five gases, NO<sub>2</sub> exhibits the most prominent ICOHP values on Cu-C<sub>2</sub>N<sub>1</sub> and Ag-C<sub>2</sub>N<sub>1</sub>. Therefore, this result substantiates the clear advantage of competitive adsorption for NO<sub>2</sub> on Cu-C<sub>2</sub>N<sub>1</sub>.

**2.2.2 Electrical response behavior.** The selectivity is the most crucial performance indicator for gas sensors. Based on our previous work,<sup>19,47,48</sup> the DOS at the Fermi level can

effectively represent the material's conductivity. Therefore, the electrical response behavior induced by the adsorption of various gases on the Cu/Ag-C<sub>2</sub>N<sub>1</sub> monolayer is comprehensively analyzed. Detailed calculation results are presented in Fig. S19 and S20.† To visually determine which material exhibits the best selective performance, all electrical response values are optimized to obtain the selectivity index shown in Fig. 5. This selectivity is derived from the comparison of the electrical conductivity before and after gas adsorption. If the conductivity remains unchanged, it indicates that the gas has no effect on the material. Conversely, any change suggests that the material demonstrates a sensitive response to the gas.

In Fig. 5, the conductivity of NO<sub>2</sub> adsorption was significantly higher than that of the background, leading to a higher electron count near this level, ultimately enhancing conductivity. In the context of NO<sub>2</sub> adsorption, the redistribution of charges is the primary driver behind this shift, causing a significant alteration in conductivity. The C<sub>2</sub>N<sub>1</sub> monolayer modified with metal atoms (Ag and Cu) displays a selective response to NO<sub>2</sub> gas amidst various other gases (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, PF<sub>5</sub>, H<sub>2</sub>O, and NH<sub>3</sub>). Notably, the DOS for all orbitals on the right side of the Cu-C<sub>2</sub>N<sub>1</sub>-NO<sub>2</sub> Fermi level surpasses that of Ag-C<sub>2</sub>N<sub>1</sub>-NO<sub>2</sub>, indicating a more robust response of Cu-C<sub>2</sub>N<sub>1</sub> to NO<sub>2</sub> compared to its Ag-C<sub>2</sub>N<sub>1</sub> counterpart.

The discernible charge transfer path is directly reflected in the DOS alteration seen in Fig. S19 and S20.† The conductivity of C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>O, and NH<sub>3</sub> on the monolayer of Ag-C<sub>2</sub>N<sub>1</sub> changed little after adsorption, and the conductivity decreased slightly after PF<sub>5</sub> adsorption. The conductivity of C<sub>2</sub>H<sub>6</sub>, PF<sub>5</sub>, H<sub>2</sub>O and NH<sub>3</sub> on the monolayer of Cu-C<sub>2</sub>N<sub>1</sub> did not change significantly after adsorption, but the conductivity of C<sub>2</sub>H<sub>4</sub> decreased slightly. There was no significant change in the conductivity of the gas after adsorption, which was consistent with the observed trend. Observing the changes of the DOS before and after adsorption of H<sub>2</sub>O in Fig. S19 and S20d,† it can be found that the DOS curves before and after adsorption change very small, and there is no change at the Fermi level, which indicates that Ag-C<sub>2</sub>N<sub>1</sub> and Cu-C<sub>2</sub>N<sub>1</sub> have no electrical signal response to H<sub>2</sub>O and the monolayer is hydrophobic. Interestingly, when NO<sub>2</sub> is adsorbed on the monolayer of Ag-C<sub>2</sub>N<sub>1</sub> and Cu-C<sub>2</sub>N<sub>1</sub>, the Cu/Ag-C<sub>2</sub>N<sub>1</sub> monolayer conductivity increases significantly, which is reflected in the obvious rise and left shift of the DOS curve at the Fermi level after NO<sub>2</sub> adsorption in the DOS diagram. This is in contrast to the DOS changes after adsorption

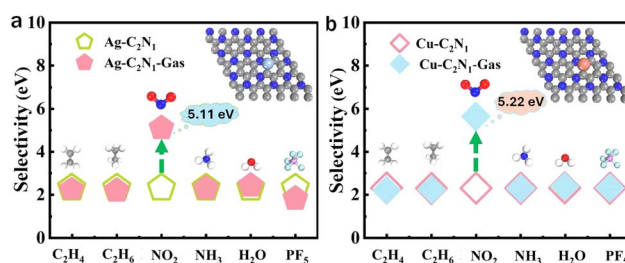


Fig. 5 Selectivity of gases on the (a) Ag-C<sub>2</sub>N<sub>1</sub> and (b) Cu-C<sub>2</sub>N<sub>1</sub> monolayers.

of other gases. It is proved that the monolayers of Ag-C<sub>2</sub>N<sub>1</sub> and Cu-C<sub>2</sub>N<sub>1</sub> can generate a selective electrical signal response to NO<sub>2</sub> gas. It is worth noting that the DOS change of NO<sub>2</sub> on the monolayer of Cu-C<sub>2</sub>N<sub>1</sub> is more obvious than that of Ag-C<sub>2</sub>N<sub>1</sub>, which proves that Cu-C<sub>2</sub>N<sub>1</sub> has a stronger effect on NO<sub>2</sub> and has a better effect.

In order to explore the reason why Cu/Ag-C<sub>2</sub>N<sub>1</sub> can respond selectively to NO<sub>2</sub> but not to the other five gases, the adsorption mechanism was explored by PDOS. The PDOS distribution analysis showed that the more overlapping peaks in different orbitals, the stronger the hybridization between the orbitals, as shown in Fig. S19 and S20.† The conspicuous overlap observed between the metal (Ag and Cu) d-orbitals and N p-orbitals substantiates strong chemical interactions between NO<sub>2</sub> and Ag-C<sub>2</sub>N<sub>1</sub>, as well as Cu-C<sub>2</sub>N<sub>1</sub>. Conversely, for the remaining five gases (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, PF<sub>5</sub>, H<sub>2</sub>O, and NH<sub>3</sub>), which exhibit weak adsorption on Ag-C<sub>2</sub>N<sub>1</sub> and Cu-C<sub>2</sub>N<sub>1</sub>, their PDOS plots indicate limited interactions. In addition, the interaction between NO<sub>2</sub> and Ag-C<sub>2</sub>N<sub>1</sub> is weak, evident from the small overlapping region between Ag-d and N-p orbitals. However, during the adsorption of NO<sub>2</sub>, the hybridization between the p orbital of the N atom and the d orbital of the Cu atom is significantly enhanced, resulting in a significant increase of the PDOS of the d orbital of the Cu atom at the Fermi level, which ultimately affects the overall electrical response of the material. In summary, compared with Ag-C<sub>2</sub>N<sub>1</sub>, Cu-C<sub>2</sub>N<sub>1</sub> has the most obvious response to NO<sub>2</sub> selective electrical signals and has the best effect.

Notably, the conductivity of H<sub>2</sub>O adsorbed on the Cu/Ag-C<sub>2</sub>N<sub>1</sub> monolayer changes very little, as depicted in Fig. 5, and no discernible changes were observed. In Fig. S19 and S20,† the overlap between the metal (Ag and Cu) d orbital and the O p orbital is still small. This observation supports the conclusion that NO<sub>2</sub> can be selectively detected by Ag-C<sub>2</sub>N<sub>1</sub> and Cu-C<sub>2</sub>N<sub>1</sub>, affirming that humidity does not impede the selective electrical signal response of the doped monolayer to NO<sub>2</sub> in multifarious gas environments.

### 2.3 Applications of gas sensors

In this section, firstly, based on the detailed discussion of high sensitivity and selectivity to NO<sub>2</sub>, the gas sensor is shown in actual usage scenarios, while also showcasing the high humidity resistance of the Cu-C<sub>2</sub>N<sub>1</sub> monolayer. Subsequently, as a response to the various hazardous gases generated after the battery becomes thermally unstable, it is imperative to conduct a thorough assessment of the operational environment to determine the temperature tolerance of high-performance sensors. Furthermore, the gas diffusion performance of gas-sensitive materials, which determines their responsiveness, is evaluated comprehensively through molecular dynamics simulations to assess the diffusion behavior of the six gases. Finally, the desorption time of the detected gases from the gas-sensitive material is analyzed.

In Fig. 6a, the practicality of Cu-C<sub>2</sub>N<sub>1</sub> and Ag-C<sub>2</sub>N<sub>1</sub> monolayer is illustrated when exposed to a range of gases emitted due to battery instability. This exposure highlights their distinctive

capacity for selectively adsorbing NO<sub>2</sub>, notably emphasized within Cu-C<sub>2</sub>N<sub>1</sub>. Both monolayers exhibit commendable hydrophobic properties. Additionally, considering the impact of temperature on the material's performance, it is essential to analyze the Gibbs free energy of the material to assess the practical temperature range for its use. The detailed calculation process can be referred to the ESI.†

The more negative the free energy, the more likely a spontaneous adsorption occurs. This study calculates Gibbs free energy at various temperatures to identify intervals where the free energy is below zero. Therefore, the actual applicable temperature range of Ag-C<sub>2</sub>N<sub>1</sub> and Cu-C<sub>2</sub>N<sub>1</sub> is determined. Fig. 6b and c show the linear relationship between the Gibbs free energy and temperature of the six gases adsorbed on Cu/Ag-C<sub>2</sub>N<sub>1</sub> at different temperatures. In Fig. 6b,  $\Delta G < 0$  is observed at a minimum temperature of 500 K, indicating that Ag-C<sub>2</sub>N<sub>1</sub> cannot adsorb certain gases at temperatures higher than 500 K. Meanwhile, Fig. 6c displays  $\Delta G < 0$  at a minimum temperature of 600 K. Consequently, the high-temperature resistance of Cu-C<sub>2</sub>N<sub>1</sub> to the adsorption of the six gases surpasses that of Ag-C<sub>2</sub>N<sub>1</sub>. Therefore, the application scope of Cu-C<sub>2</sub>N<sub>1</sub> is broader. Selective detection of NO<sub>2</sub> on Cu-C<sub>2</sub>N<sub>1</sub> in high-temperature environments is superior and applicable over a wider temperature range compared to Ag-C<sub>2</sub>N<sub>1</sub>. The noteworthy aspect is the maximum applicable temperature of 500 K on Ag-C<sub>2</sub>N<sub>1</sub> and 600 K on Cu-C<sub>2</sub>N<sub>1</sub>, which are the upper limits for H<sub>2</sub>O adsorption. The results of DOS analysis confirmed that humidity has no impact on the selective adsorption performance. Consequently, the actual response temperature upper limit of Ag-C<sub>2</sub>N<sub>1</sub> is 700 K (determined by Ag-C<sub>2</sub>N<sub>1</sub>-PF<sub>5</sub>), while for Cu-C<sub>2</sub>N<sub>1</sub>, it's 800 K (determined by Cu-C<sub>2</sub>N<sub>1</sub>-C<sub>2</sub>H<sub>6</sub>). The Cu-C<sub>2</sub>N<sub>1</sub> monolayer's applicable temperature surpasses the hot mixture's maximum temperature released after battery damage (470 to 720 K) and remains minimally affected by humidity, making it suitable for a wide range of environments.

For the gas diffusion performance of Cu/Ag-C<sub>2</sub>N<sub>1</sub>, molecular dynamics simulations were used to calculate the diffusion coefficient. The detailed calculation can be found in the ESI.† The diffusion coefficient plays a critical role as it quantifies the gas's diffusion capacity. A larger diffusion coefficient corresponds to a faster diffusion rate, indicating a lower energy barrier required for diffusion.<sup>62,63</sup> In order to explore the diffusion behavior of gases on the monolayer, the diffusion coefficients of the six gas molecules on the monolayer were calculated. The initial and the final stable configurations are shown in Fig. S21 and S22.† Cu-C<sub>2</sub>N<sub>1</sub>-NO<sub>2</sub> has the smallest diffusion coefficient as shown in Table S2,† which further proved that the monolayer of Cu-C<sub>2</sub>N<sub>1</sub> can achieve selective adsorption of NO<sub>2</sub> gas. Interestingly, the diffusion coefficient of water is the largest, indicating that the monolayer does not attract much water.

NO<sub>2</sub> exhibits the lowest diffusion rate on the monolayer. To comprehend its underlying mechanism from a physicochemical perspective, NO<sub>2</sub> diffusion activation energy was obtained by fitting the Arrhenius equation according to the diffusion coefficient. The detailed calculation can be referred to the ESI.† The stable structures of Cu-C<sub>2</sub>N<sub>1</sub>-NO<sub>2</sub> at different temperatures

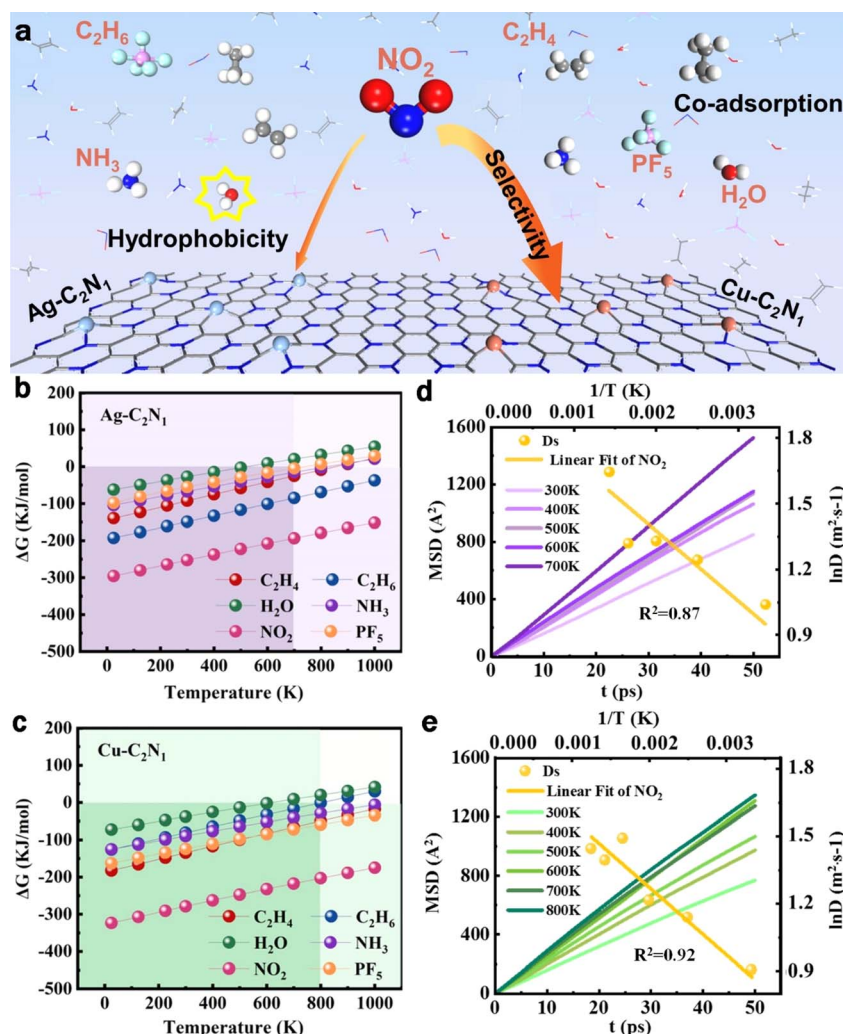


Fig. 6 (a) Schematic diagram of the high selectivity and hydrophobicity of Cu/Ag-C<sub>2</sub>N<sub>1</sub>. The Gibbs free energy of the six gases on (b) Ag-C<sub>2</sub>N<sub>1</sub> and (c) Cu-C<sub>2</sub>N<sub>1</sub> as a function of temperature. Gas diffusion and mean-squared displacement on (d) Ag-C<sub>2</sub>N<sub>1</sub> and (e) Cu-C<sub>2</sub>N<sub>1</sub> at different temperatures.

are shown in Fig. S23 and S24.† The level of activation energy directly affects both the difficulty and the rate of adsorption in the process.<sup>64,65</sup> The smaller the activation energy, the less energy is required, making the adsorption more likely to occur. As shown in Fig. 6d and e, the mean-squared displacement of NO<sub>2</sub> on Ag/Cu-C<sub>2</sub>N<sub>1</sub> in the effective applicable temperature range shows that the diffusion activation energy of Cu-C<sub>2</sub>N<sub>1</sub> (2.5 kJ mol<sup>-1</sup>) is less than that of Ag-C<sub>2</sub>N<sub>1</sub> (2.7 kJ mol<sup>-1</sup>). Thus, it is confirmed that Cu-C<sub>2</sub>N<sub>1</sub> has more advantages than Ag-C<sub>2</sub>N<sub>1</sub> in the field of NO<sub>2</sub> detection.

In the practical sensor usage, assessing gas molecule recovery time performance is crucial. The recovery time ( $\tau$ ) is defined as the time taken by a sensor to return to its original state, when the gas is removed. According to transition state theory,  $\tau$  is calculated as:<sup>16</sup>

$$\tau = \nu^{-1} e^{-E_{\text{ads}}/kT} \quad (4)$$

where  $\nu$  is the attempt frequency (determined to be  $10^{12} \text{ s}^{-1}$ ),  $k$  represents the Boltzmann constant, and  $T$  is the temperature.

Tables S4 and S5† detail the  $\tau$  of the six gases (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, NH<sub>3</sub>, NO<sub>2</sub>, H<sub>2</sub>O, and PF<sub>5</sub>) adsorbed on the monolayers at varied temperatures. Overall, as temperatures rise, the  $\tau$  decreases, indicating accelerated gas desorption. The Cu-C<sub>2</sub>N<sub>1</sub> monolayer exhibits longer desorption times compared to Ag-C<sub>2</sub>N<sub>1</sub>, with NO<sub>2</sub> displaying prolonged  $\tau$  due to its robust adsorption energy, aligning with experimental observations.<sup>26</sup> Notably, in scenarios of battery damage and high-temperature gas release, the Cu-C<sub>2</sub>N<sub>1</sub> monolayer continues to exhibit high selectivity to NO<sub>2</sub>, demonstrating its advanced nature.

### 3 Conclusions

In summary, the gas-sensitive behavior on Cu/Ag-C<sub>2</sub>N<sub>1</sub> was clarified by dispersion-corrected DFT calculations. The results show that Cu and Ag can be anchored to the monolayer of the C<sub>2</sub>N<sub>1</sub> material. After doping metal atoms, the cohesion energy was compared to illustrate the monolayer stability. By DOS analysis, Cu decorated C<sub>2</sub>N<sub>1</sub> improved conductivity better than the Ag atom. Moreover, NO<sub>2</sub> prefers to adsorb on Cu-C<sub>2</sub>N<sub>1</sub> due

to its obvious electronic overlap. The adsorption energy of NO<sub>2</sub> for Cu-C<sub>2</sub>N<sub>1</sub> is -3.54 eV, and that of NO<sub>2</sub> for Ag-C<sub>2</sub>N<sub>1</sub> is -3.27 eV. The adsorption of NO<sub>2</sub> by Cu-C<sub>2</sub>N<sub>1</sub> is significant as also demonstrated by charge transfer, bond length and COHP. Thus, Cu-C<sub>2</sub>N<sub>1</sub> has a stronger affinity for NO<sub>2</sub>. Notably, we clearly show for the first time in the DOS analysis that Cu-C<sub>2</sub>N<sub>1</sub> achieves a single electrical response to NO<sub>2</sub> while eliminating other gaseous disturbances. Furthermore, we also use d-band-center theory to understand the underlying mechanism of gas adsorption on the Cu/Ag-C<sub>2</sub>N<sub>1</sub> monolayer. In terms of practicality, the temperature application range of the modified Cu-C<sub>2</sub>N<sub>1</sub> (<800 K) is higher than that of Ag-C<sub>2</sub>N<sub>1</sub> (<700 K). Interestingly, the adsorption and response of H<sub>2</sub>O were extremely poor, demonstrating the minimal effect of humidity on the monolayer. Molecular dynamics simulations revealed that the fundamental reason for the difference in the diffusion performance of NO<sub>2</sub> on the monolayers is that Cu-C<sub>2</sub>N<sub>1</sub> has a lower diffusion activation energy barrier (2.5 kJ mol<sup>-1</sup>). When considering cost, Cu proves to be considerably more economical than Ag. Our research confirms that Cu-C<sub>2</sub>N<sub>1</sub> surpasses the Ag-C<sub>2</sub>N<sub>1</sub> in both adsorption and response to NO<sub>2</sub> gas. Thus, the Cu-C<sub>2</sub>N<sub>1</sub> monolayer can be used as a gas sensor for gas generated by degassed products, greatly increasing the chances of successfully developing a new prototype of safety monitoring.

## Data availability

Data will be made available on request.

## Author contributions

Mingyang Gu: data curation, formal analysis, investigation, methodology, writing – original draft, and writing – review & editing. Lin Tao: validation, data curation, methodology, supervision, funding acquisition, conceptualization, validation, and writing – review & editing. Davoud Dastan: methodology, supervision, and resources. Jie Dang: methodology, formal analysis, and software. Timing Fang: methodology, formal analysis, and software. Baigang An: supervision, formal analysis, and writing – review & editing.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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