# Tuning the Electrochemical Stability of Carbon Based Single-Atom Structures via Doping: Trade-off Electrosorption/Leaching Behavior

Xu Zhang, [ab] Lin Tao,[a]* Davoud Dastan,[c] Hongwei Zhang,[b] and Baochang Gao[b]*

[a] *School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, P. R. China.*

[b] *Institute of Phytochemistry, Daqing Branch of Heilongjiang Academy of Sciences, Daqing 163316, P. R. China.*

[c] *Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14850, USA*

* Corresponding author E-mail: taolin@ustl.edu.cn; chemgbc@163.com.

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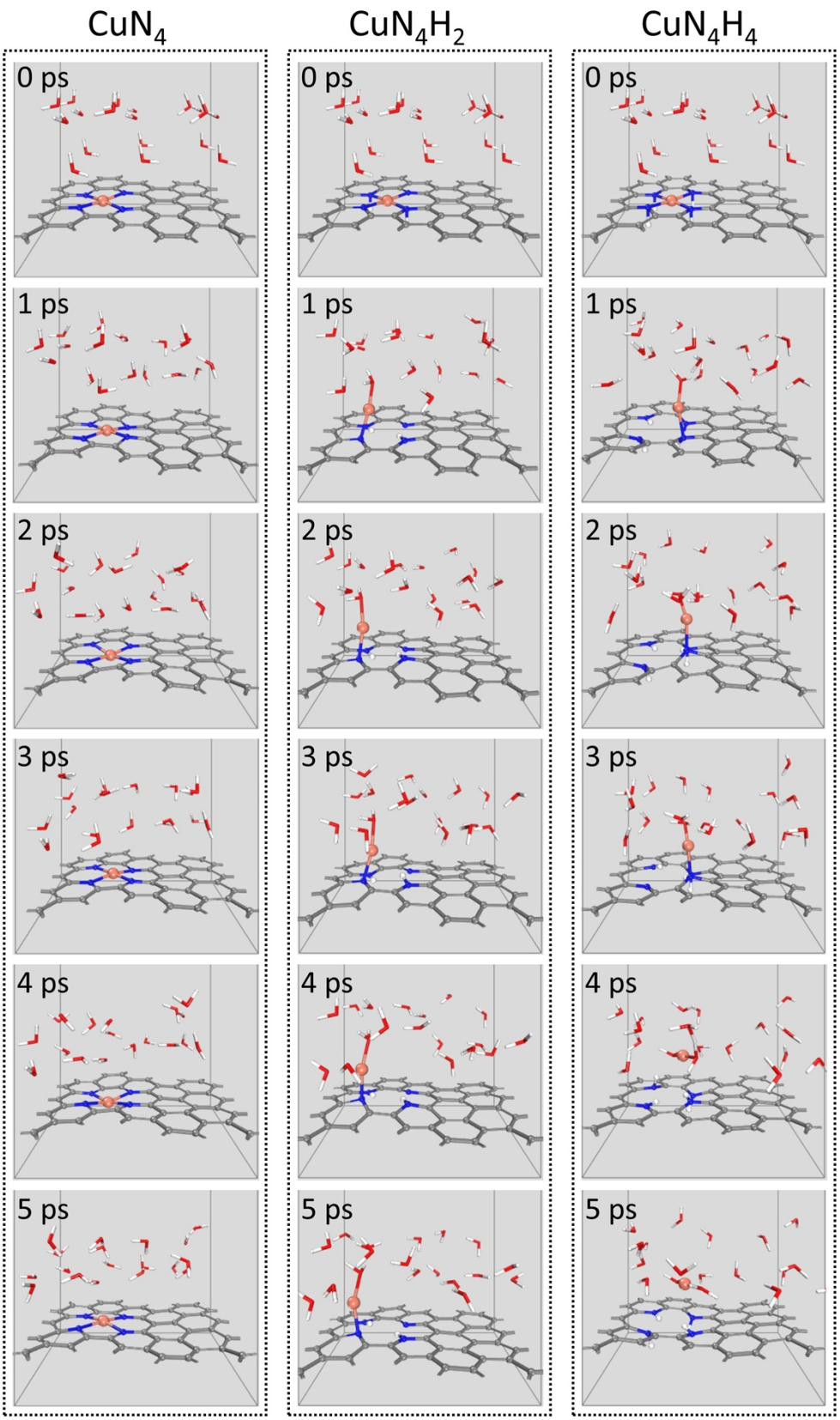


**Figure S1**. Snapshot of 5 ps simulation of $CuN_4$, $CuN_4H_2$, and $CuN_4H_4$ structures at 298.15 K.

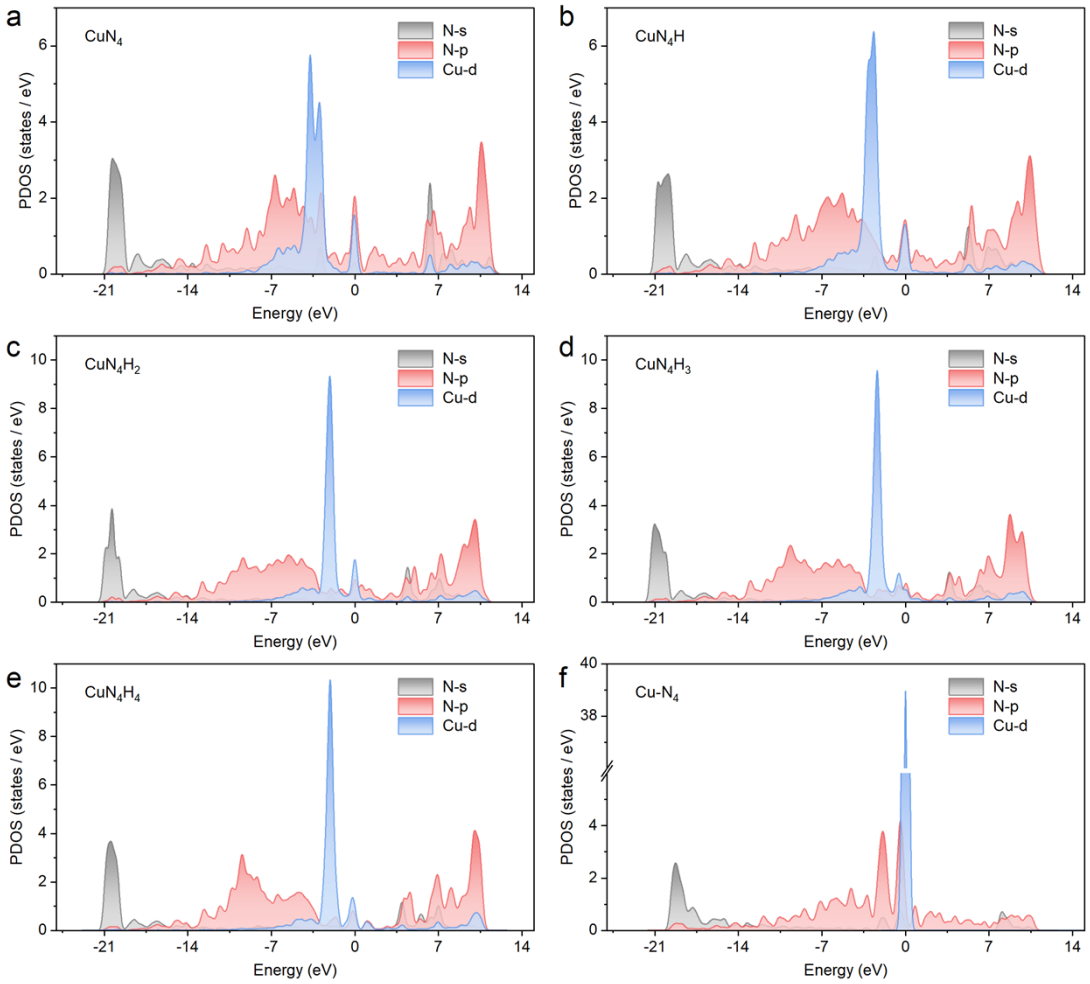


**Figure S2**. PDOS of $CuN_4$ structures with different numbers of adsorbed protons and leached copper atoms.

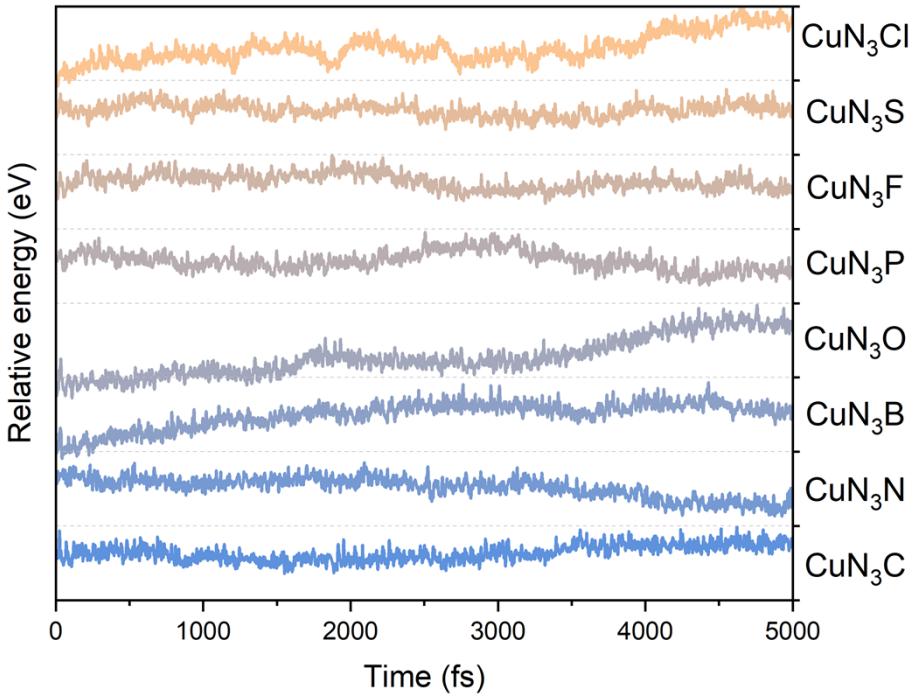


**Figure S3**. Energy time-dependent curves of the 5 ps dynamic simulation process.

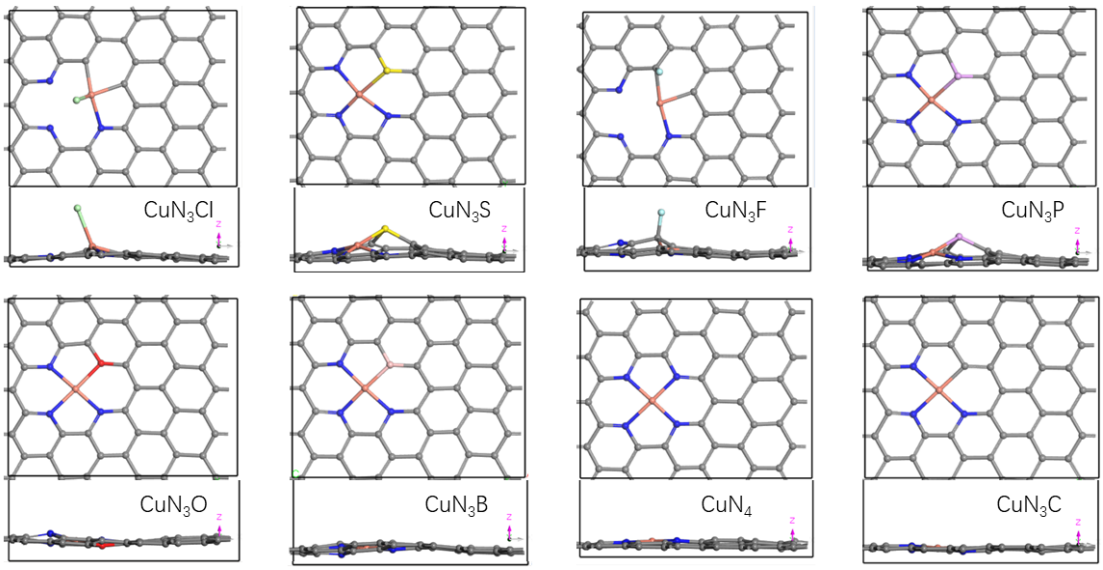


**Figure S4**. The top and front views of the structures after 5 ps dynamic simulation, among them, gray: C, blue: N, orange: Cu, light green Cl, yellow S, light blue F, light purple P, red O, light pink B.

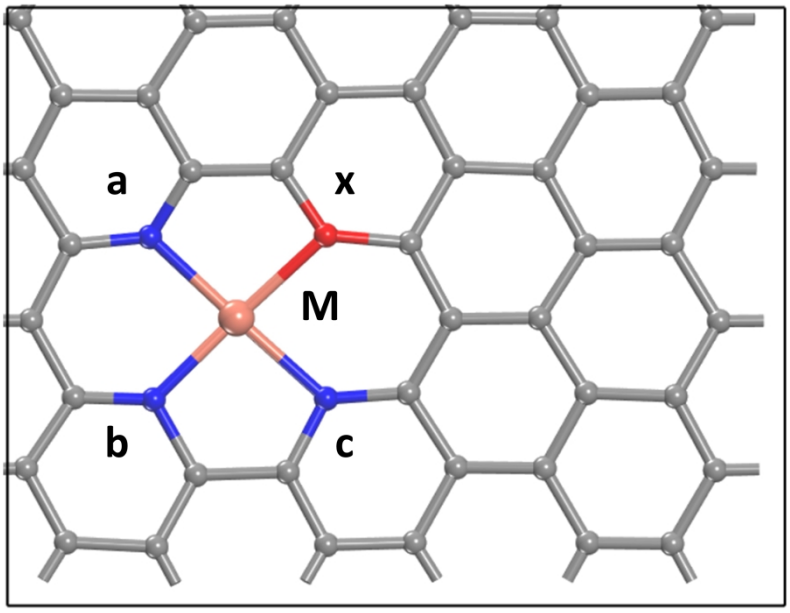


**Figure S5**. Model schematic diagram, where X represents doping site, and a, b, and c correspond to corresponding N sites.

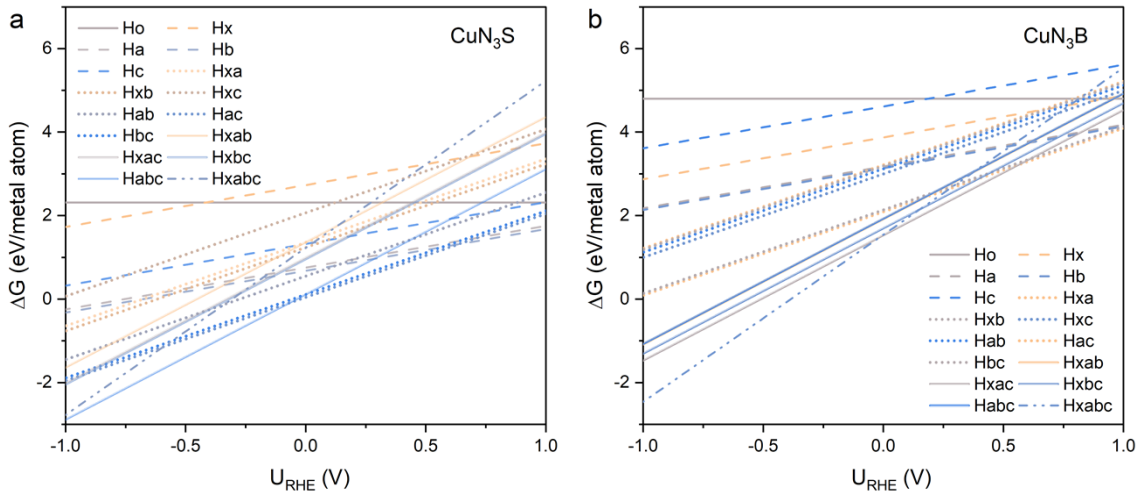


**Figure S6.** Surface phase diagram of copper leaching with different adsorption configurations of $CuN_3B$ and $CuN_3S$.

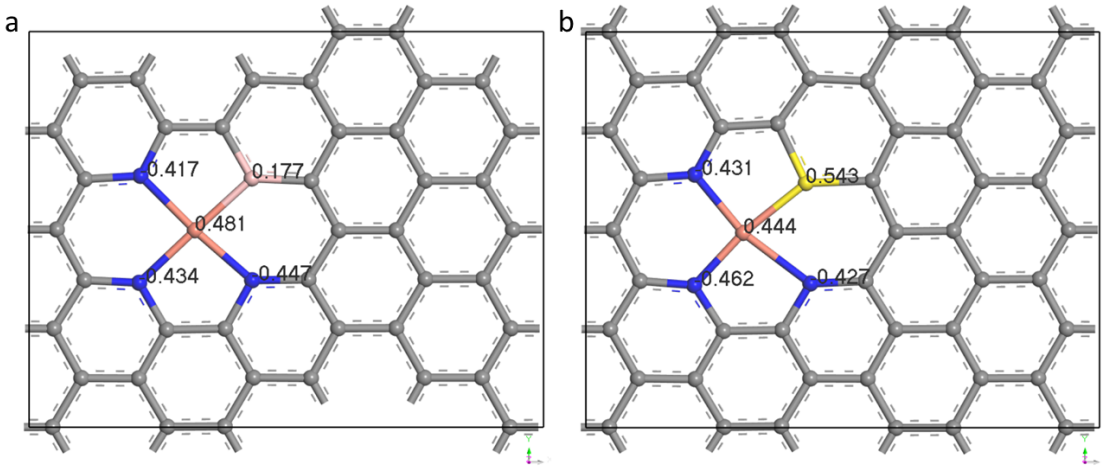


**Figure S7.** Mulliken charge analysis of (a) $CuN_3B$ and (b) $CuN_3S$.

Compared to Bader charges based on topological partitioning of electron density, Mulliken charges, which are based on the allocation of molecular orbital coefficients, are more sensitive to the choice of basis set. However, they still hold value for qualitative analysis.

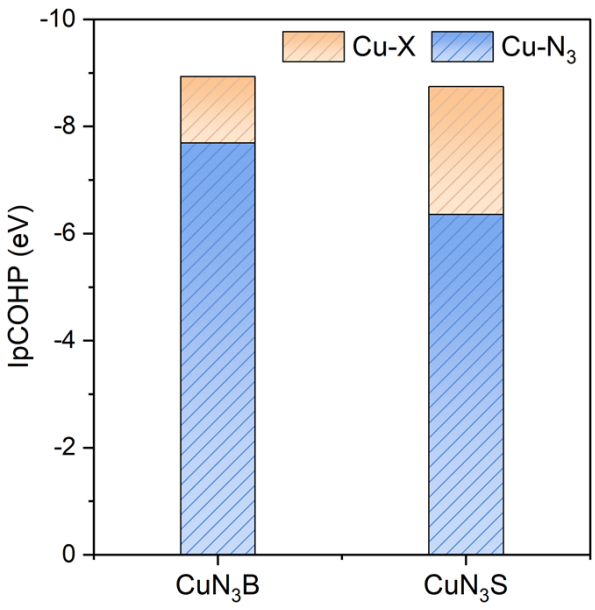


**Figure S8**. The IpCOHP contribution allocation of Cu-$N_3$X.

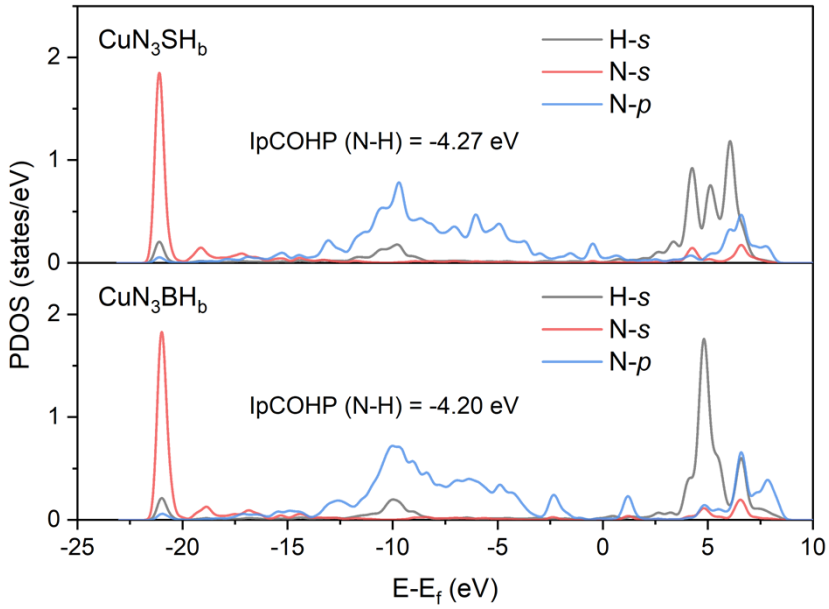


**Figure S9**. N-H IpCOHP of $CuN_3BH_b$ and $CuN_3SH_b$.

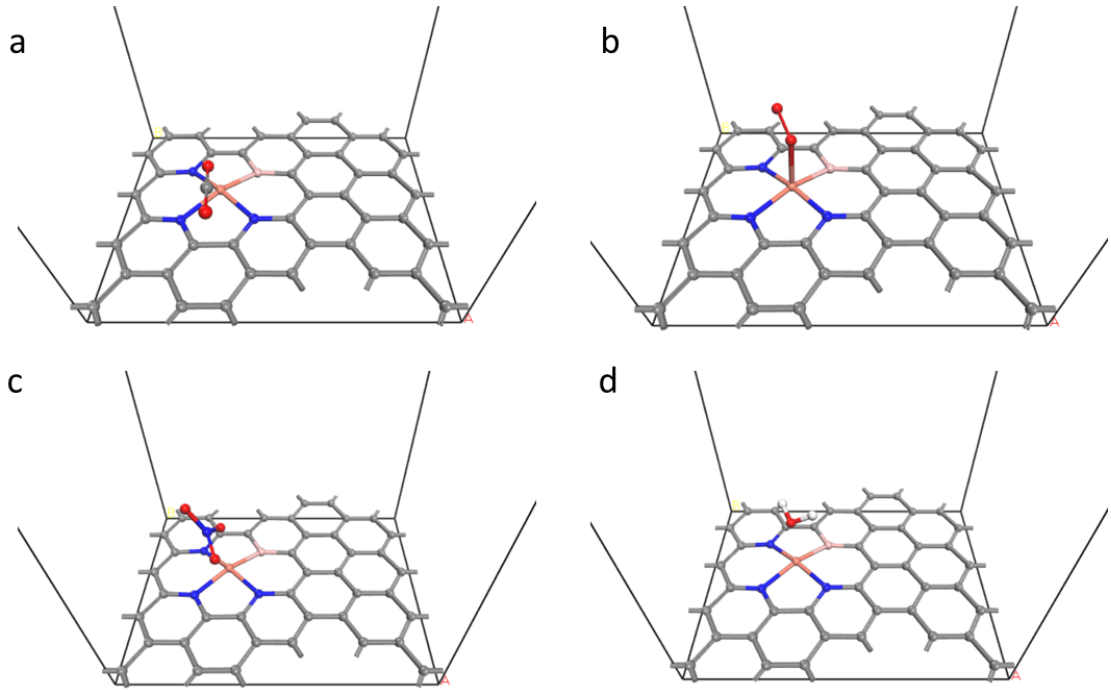


**Figure S10**. Molecular adsorption model on $CuN_3B$. (a) $CO_2$, (b) $O_2$, (c) $NO_3^-$, and (d) $H_2O$.

**Table S1.** The cumulative proton adsorption energy, Cu leaching energy after proton adsorption, and the corresponding zero-point energy corrections on $CuN_3B$.

| | $E_{Culea}$ | $E_{Hads}$ | $\Delta E_{ZPE}$ of $E_{Culea}$ | $\Delta E_{ZPE}$ of $E_{Hads}$ |
|---|---|---|---|---|
| $H_b$ | 2.65 | 1.15 | 0.02 | 0.05 |
| $H_{xa}$ | 2.11 | 1.31 | 0.01 | 0.07 |
| $H_{ac}$ | 1.93 | 2.61 | 0.00 | 0.12 |
| $H_{xabc}$ | 1.08 | 3.09 | 0.00 | 0.18 |

*Unit: eV

**Table S2.** Cumulative proton adsorption energy of $CuN_3X$.

| | $CuN_3S$ | $CuN_3P$ | $CuN_3O$ | $CuN_3B$ | $CuN_4$ | $CuN_3C$ |
|---|---|---|---|---|---|---|
| $H_x$ | -0.67915* | -1.56199 | 2.25206 | 0.1108 | 0.58084 | -0.41152 |
| $H_a$ | -1.17438 | -1.07229 | 0.57273 | 1.22095 | 0.58084 | 0.62296 |
| $H_b$ | -1.3289 | -1.23932 | 0.50054 | 1.1505 | 0.58084 | 0.64263 |
| $H_c$ | -0.94558 | -0.96087 | 0.63972 | 1.19298 | 0.58084 | 0.54593 |
| $H_{xa}$ | 0.03751 | -1.09116 | 2.73233 | 1.30092 | 1.10481 | 0.16559 |
| $H_{xb}$ | -0.11673 | -0.90481 | 2.58358 | 1.29004 | 1.15171 | 0.28087 |
| $H_{xc}$ | 0.0136 | -0.87964 | 2.95326 | 1.51965 | 1.10481 | 0.19342 |
| $H_{ab}$ | -0.43665 | -0.3651 | 1.299 | 2.56643 | 1.15171 | 1.32414 |
| $H_{ac}$ | -0.35797 | -0.36499 | 0.69088 | 2.60479 | 1.10481 | 1.23106 |
| $H_{bc}$ | -1.07236 | -0.8517 | 0.97785 | 2.58651 | 1.15171 | 1.18401 |
| $H_{xab}$ | 0.75535 | -0.34223 | 3.55268 | 2.64512 | 1.85472 | 0.88685 |
| $H_{xac}$ | 0.70022 | -0.32833 | 2.91907 | 2.73328 | 1.85472 | 0.77148 |
| $H_{xbc}$ | 0.63459 | -0.23848 | 3.25453 | 2.62493 | 1.85472 | 0.83599 |
| $H_{abc}$ | 0.38702 | 0.38016 | 1.929 | 2.89063 | 1.85472 | 1.86538 |
| $H_{xabc}$ | 1.53562 | 0.45799 | 4.66684 | 3.09734 | 2.65551 | 1.50055 |

*Unit: eV

**Table S3.** Cu leaching energy after proton adsorption on $CuN_3X$.

| | $CuN_3S$ | $CuN_3P$ | $CuN_3O$ | $CuN_3B$ | $CuN_4$ | $CuN_3C$ |
|---|---|---|---|---|---|---|
| $H_0$ | 2.3143* | 3.12569 | 3.69498 | 4.79963 | 5.2039 | 5.99922 |
| $H_x$ | 3.40948 | 4.19467 | 0.20121 | 4.42083 | 2.76812 | 3.94356 |
| $H_a$ | 1.93093 | 2.23403 | 1.34096 | 2.61414 | 2.76812 | 3.63888 |
| $H_b$ | 2.00861 | 2.30072 | 1.37682 | 2.64685 | 2.76812 | 3.59853 |
| $H_c$ | 2.26881 | 2.99857 | 1.81529 | 4.08031 | 2.76812 | 2.98609 |
| $H_{xa}$ | 1.31941 | 2.03244 | -1.60151 | 2.10964 | 0.72484 | 1.83026 |
| $H_{xb}$ | 1.3535 | 1.85893 | -1.38131 | 2.16506 | 0.59919 | 1.66719 |
| $H_{xc}$ | 2.05263 | 2.577 | 1.41872 | 2.79764 | 0.72484 | 2.37013 |
| $H_{ab}$ | 0.98773 | 1.1127 | 0.55865 | 1.87376 | 0.59919 | 2.75288 |
| $H_{ac}$ | 0.40204 | 1.11262 | 0.44138 | 1.92739 | 0.72484 | 0.76435 |
| $H_{bc}$ | 1.18298 | 1.66877 | 0.22314 | 1.91798 | 0.59919 | 0.76353 |
| $H_{xab}$ | 0.60929 | 1.02604 | -2.0972 | 1.25084 | 0.05763 | 0.94208 |
| $H_{xac}$ | 0.28893 | 0.66493 | 0.39575 | 0.77695 | -0.34746 | 0.48848 |
| $H_{xbc}$ | 0.32041 | 0.69581 | 0.02832 | 1.05072 | -0.34746 | 0.47305 |
| $H_{abc}$ | -0.27263 | 0.34773 | -0.48048 | 1.01791 | -0.34746 | -0.03477 |
| $H_{xabc}$ | -0.30964 | -0.08089 | -0.99655 | 1.08277 | -0.50178 | -0.08059 |

*Unit: eV