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Supplementary Material

Cu Dimer Anchored on C_2N Monolayer: Low-cost and Efficient Catalyst for CO Oxidation

Fengyu Li,[a] Zhongfang Chen[b,*]

[a] *School of Physical Science and Technology, Inner Mongolia University, Hohhot, 010021, China*

[b] *Department of Chemistry, University of Puerto Rico, Rio Piedras Campus, San Juan, PR 00931, USA*

*Corresponding Author: zhongfangchen@gmail.com

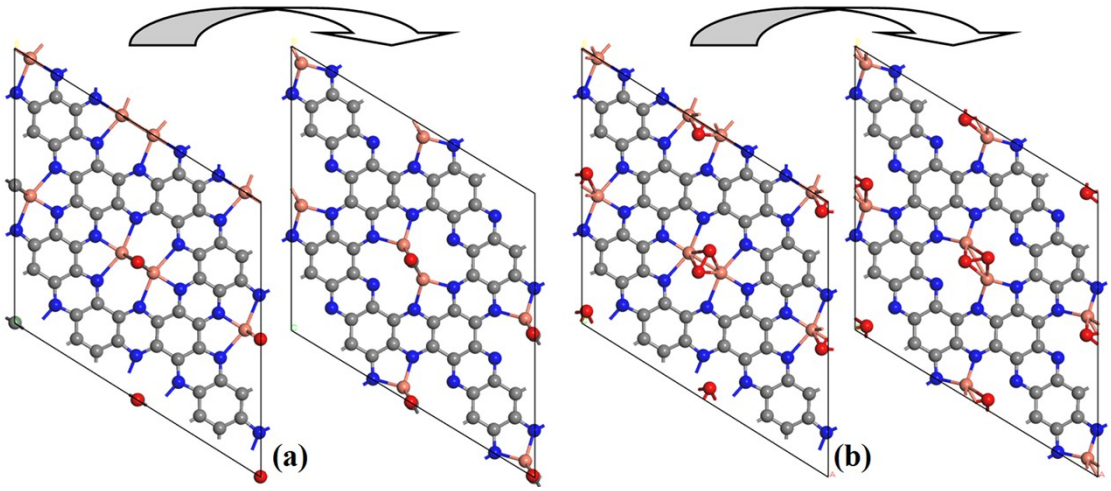

Figure S1. Top views of $Cu_2@C_2N$ structure transformation (P1P1→P2P2) after CO (a) and O_2 (b) adsorption. Color scheme: Cu, orange; C, gray; N, blue; O, red.

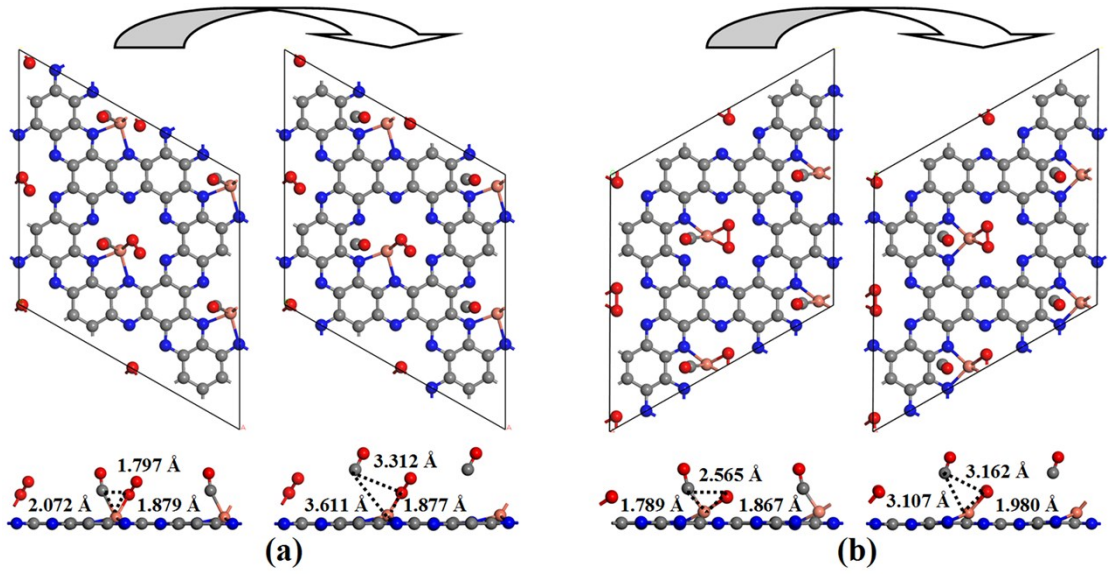

Figure S2. Interaction between coadsorbed O_2 and CO with the configuration of (a) end-on O_2 and end-on CO, (b) side-on O_2 and end-on CO on $Cu_1@C_2N$. In the initial structure (left) the CO is very close to O_2, while in the fully optimized final structure (right) the CO and O_2 are separated. Color scheme: Cu, orange; C, gray; N, blue; O, red.

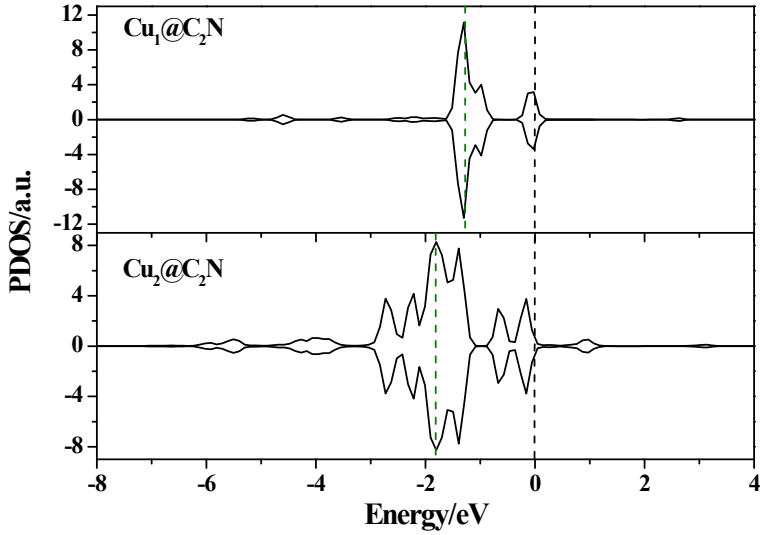

Figure S3. PDOS of Cu-3*d* of $Cu_1@C_2N$ and $Cu_2@C_2N$. The Fermi level was set to be zero as denoted by the black dashed line, and the *d*-band center was denoted by the green dashed line.

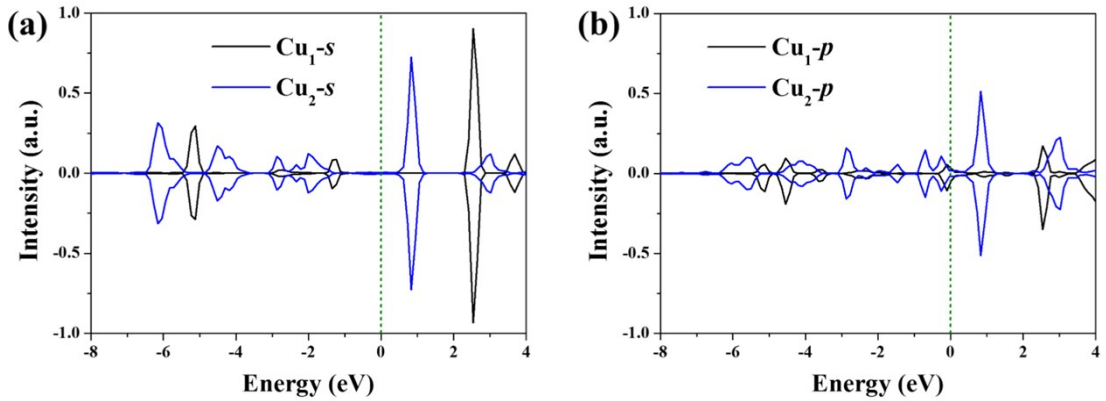

Figure S4. PDOS of Cu-*s* (a) and Cu-*p* of $Cu_1@C_2N$ (black) and $Cu_2@C_2N$ (blue). The Fermi level was set to be zero as denoted by the green dashed line.

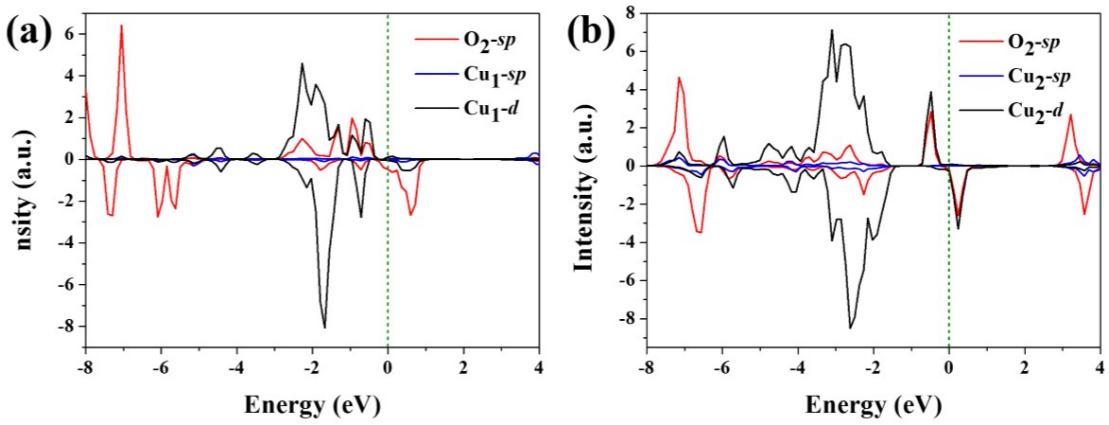

Figure S5. Partial density of states (PDOS) of O_2 adsorption on $Cu_1@C_2N$ (a) and $Cu_2@C_2N$ (b). The Fermi level was set to be zero as denoted by the green dashed line.

The details to examine the feasibility for experimental realization of $Cu_1@C_2N$ and $Cu_2@C_2N$

The following synthetic route was used to simulate the formation of $Cu_1@C_2N$ and $Cu_2@C_2N$.

$$CuCl_2 + * \rightarrow CuCl_2* \quad \text{(step 1)}$$

$$CuCl_2* + 2H_3O^+ + 2e^- \rightarrow Cu* + 2H_2O{\cdot}HCl \quad \text{(step 2)}$$

$$Cu* + CuCl_2 \rightarrow Cu*CuCl_2 \quad \text{(step 3)}$$

$$Cu*CuCl_2 + 2H_3O^+ + 2e^- \rightarrow Cu*Cu(HCl)_2 + 2H_2O \quad \text{(step 4)}$$

$$Cu*Cu(HCl)_2 \rightarrow Cu*Cu + 2HCl \quad \text{(step 5)}$$

Where the * denotes the C_2N sheet.

The step 1 associates the adsorption of $CuCl_2$ on C_2N monolayer (S1 in Figure S6), and the adsorption energy is 0.79 eV. In step 2, as the H_3O^+ groups approach Cl^- ions in the adsorbed $CuCl_2*$, the Cu−Cl bonds are elongated and eventually broken

(from the initial 2.21 and 2.19 Å to the final 3.82/3.85 and 3.74/3.76 Å, respectively), resulting in two $HCl{\cdot}H_2O$ complexes (S2 in Figure S6), and such a process is spontaneous and barrierless. The HCl groups (S3 in Figure S6) can be easily released from the surface since the binding energy of each HCl is as low as 0.01 eV, and the $Cu_1@C_2N$ (Cu*) is formed (S4 in Figure S6). Providing that each pore of C_2N monolayer is first anchored with one Cu atom, the excessive $CuCl_2$ can be adsorbed on Cu* (Cu*$CuCl_2$) with a much larger adsorption energy of 2.05 eV (step 3), the strong adsorption strength of the second $CuCl_2$ originates from the preadsorbed Cu bonding with Cu^{2+} and one Cl^- in the second $CuCl_2$ (S5 in Figure S6). The same to step 2, in step 5, the Cl^- ions in the adsorbed Cu*$CuCl_2$ interacts with H^+ ions in H_3O^+ groups to form H−Cl bonds, producing H_2O molecules (S6 in Figure S6). Finally, in step 6, the two adsorbed HCl groups (S7 in Figure S6) are released by consuming 0.37 eV energy, resulting in $Cu_2@C_2N$ (S8 in Figure S6). The strong adsorption strength of HCl groups on Cu dimer arises from the short distances between Cl and Cu (2.30 and 3.15 Å).

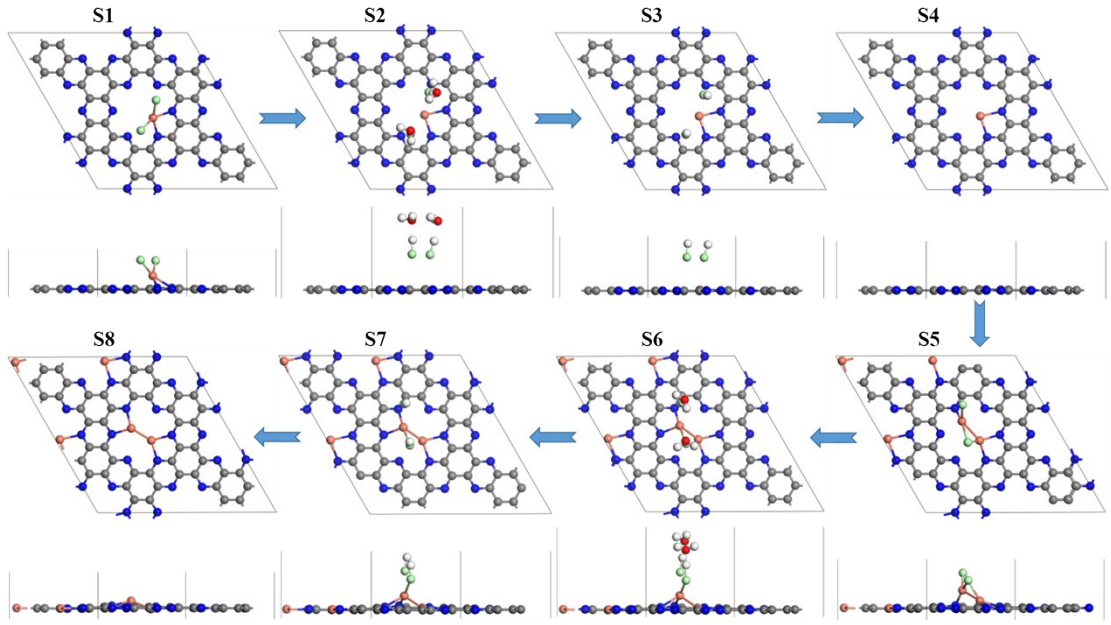

Figure S6. Top and side views of the designed synthetic route for $Cu@C_2N$.

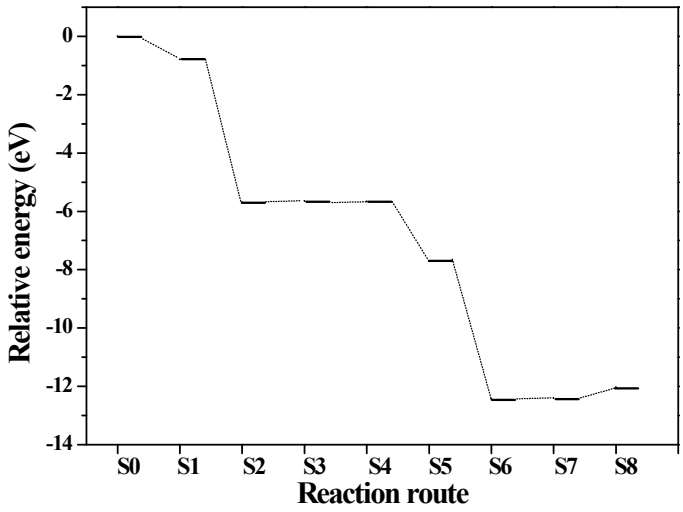

Figure S7. The energy profile of the above reaction route in Figure S6. S0 denotes the initial C_2N monolayer (a 2×2×1 supercell).

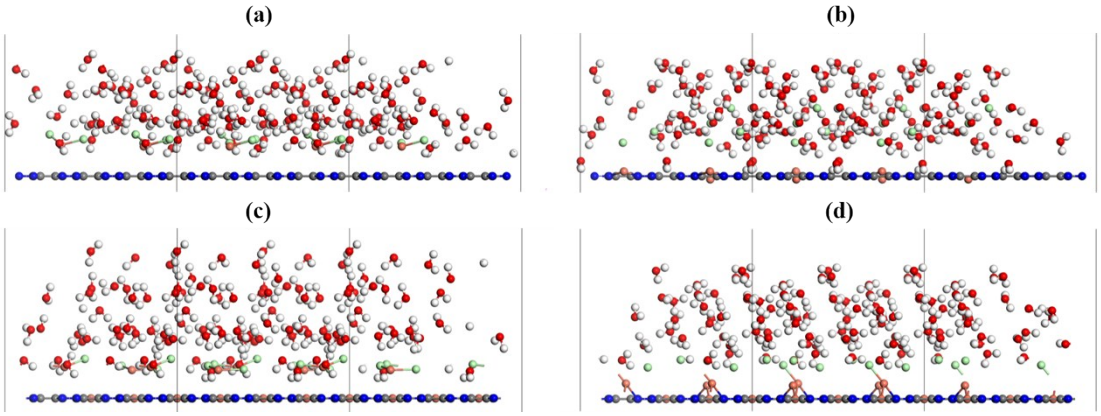

Figure S8. Side views of the snapshots of atomic configurations of FAMD simulations for the synthetic process of $Cu_1@C_2N$ (a,b) and $Cu_2@C_2N$ (c,d). The model consists of a 2×2×1 supercell of C_2N, two $CuCl_2$ molecules, and 31 H_2O molecules.