Electronic Supplementary Material for:

Effect of sulfur dioxide impurity on electrochemical reduction of carbon dioxide over Cu-based bimetal catalysts

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Table S1 DFT calculated free energy of potential limiting step in eV.

Fig**. S1** Schematic illustration of the structural model of the Cu-M (M = Cr, Fe, Mn, Ru, Os, Ir, Mo,

W, Ni and Pd) surface.

Fig. S2 Optimized structures of S elemental substance adsorption on the catalyst surface at the Hollow site.

Fig. S3 Optimized structures of COOH* over the Cu-M (M = Cr, Fe, Mn, Ru, Os, Ir, Mo, W, Ni and Pd) catalysts.

Fig. S4 Optimized structures of CO* over the Cu-M (M = Cr, Fe, Mn, Ru, Os, Ir, Mo, W, Ni and Pd) catalysts.

Free Energy Calculation

The free energies of the reaction intermediates were derived from the corresponding binding energies by adding the zero-point energy (ZPE), and entropy (−TS) corrections, which were calculated based on the vibrational frequency analysis. The computational hydrogen electrode (CHE) model was used to estimate the free energy change (ΔG) at each elementary step:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \quad \text{(S1)}$$

where E, E_{ZPE}, S, and T represent the DFT-optimized energy, zero-point energy, entropy, and temperature (298 K), respectively.

The adsorption energy (E_{ad}) is used to evaluate the interaction strength between the small molecule species and catalyst surface, and is expressed by the following formula:

$$E_{ad} = E_{(catalyst\text{-}M)} - (E_{catalyst} + E_M) \quad \text{(S2)}$$

where $E_{(catalyst\text{-}M)}$, $E_{catalyst}$, and E_M represent the total energies of the catalyst surface covered by adsorbate, the clean catalyst surface, and the unabsorbed molecules, respectively.

CO_2RR-to-CO is a two-electron-transfer process including three steps:

$$CO_2(g) + H^+ + e^- \rightarrow COOH^* \quad \text{(R1)}$$

$$COOH^* + H^+ + e^- \rightarrow CO^* + H_2O(l) \quad \text{(R2)}$$

$$CO^* \rightarrow CO(g) \quad \text{(R3)}$$

CO_2RR-to-HCOOH is also a two-electron-transfer process including two steps:

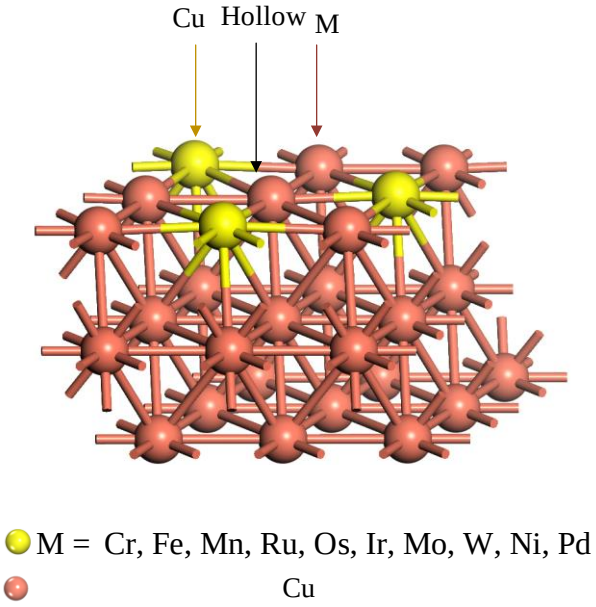
$$CO_2(g) + H^+ + e^- \rightarrow COOH^*/OCHO^* \quad \text{(R4)}$$

$$COOH^*/OCHO^* + H^+ + e^- \rightarrow HCOOH(l) \quad \text{(R5)}$$

where * denotes active site of electrocatalysts. (l) and (g) represent liquid and gaseous phases, respectively. COOH*, CO*, and OCHO* are the adsorbed-state intermediates of the CO_2RR.

Table S1 DFT calculated free energy of potential limiting step in eV.

Catalyst	Clean surface	S-doped surface
Cu-Cr	0.426	0.605
Cu-Fe	0.738	0.866
Cu-Mn	0.491	0.669
Cu-Ru	1.239	1.301
Cu-Os	1.458	1.616
Cu-Ir	1.091	1.130
Cu-Mo	1.035	1.067
Cu-W	1.251	0.528
Cu-Ni	0.803	1.165
Cu-Pd	0.780	0.446



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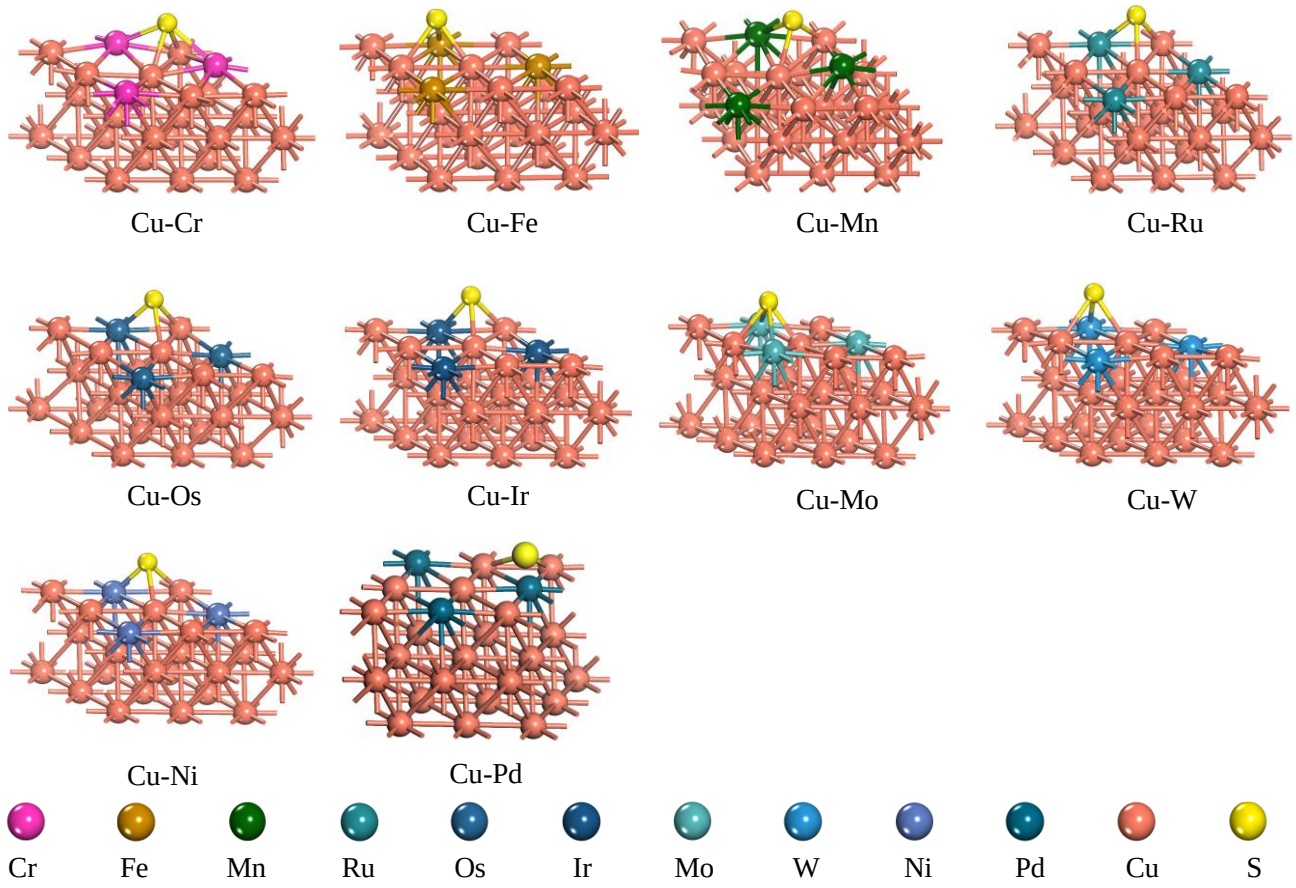

Fig. S2 Optimized structures of S elemental substance adsorption on the catalyst surface at the Hollow site.

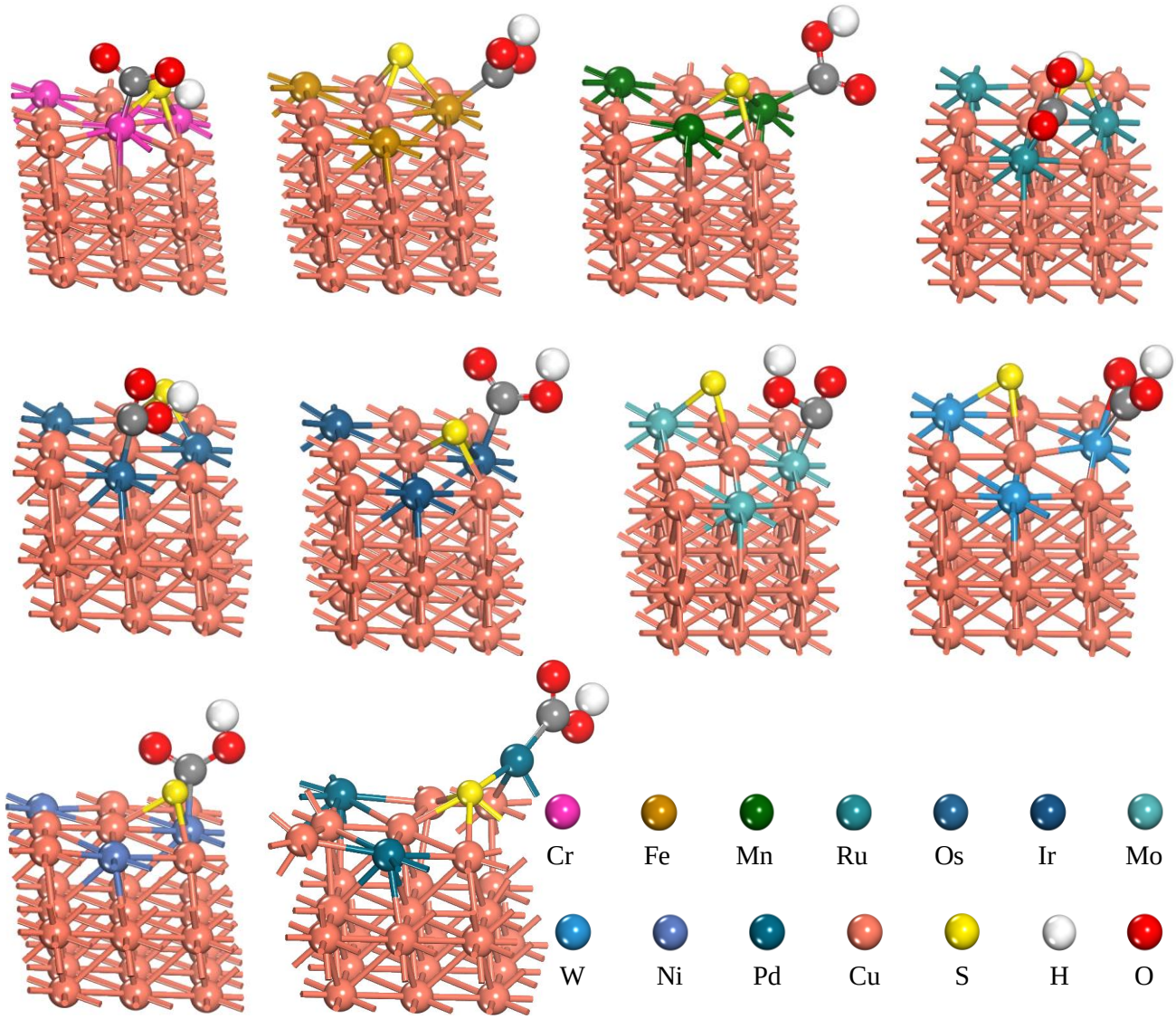

Fig. S3 Optimized structures of COOH* over the Cu-M (M = Cr, Fe, Mn, Ru, Os, Ir, Mo, W, Ni and Pd) catalysts.

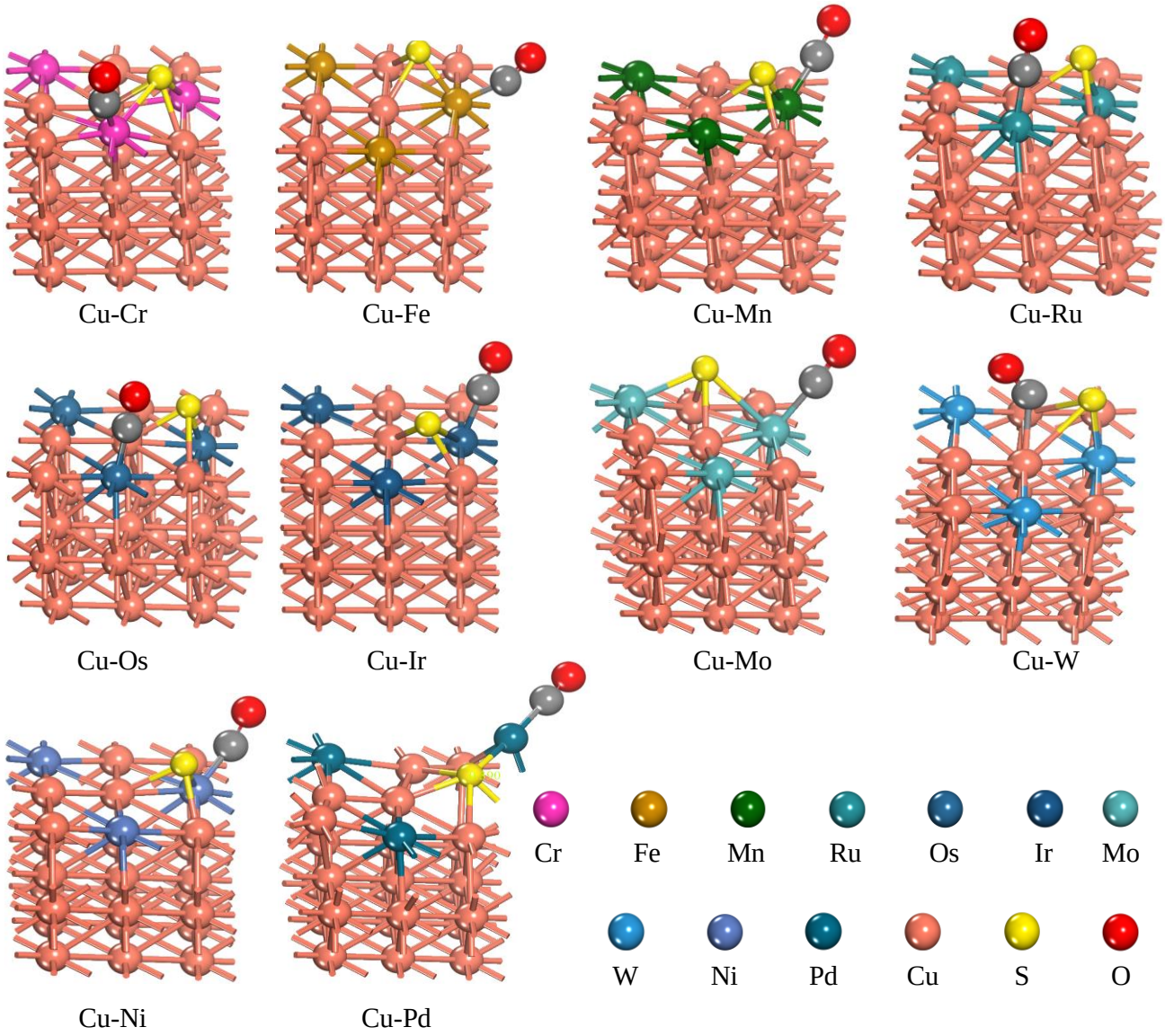

Fig. S4 Optimized structures of CO* over the Cu-M (M = Cr, Fe, Mn, Ru, Os, Ir, Mo, W, Ni and Pd) catalysts.