# Electronic Supplementary Information (ESI)

## Electrocatalytic $CO_2$ reduction reaction on dual-metal- and nitrogen-doped graphene: Coordination environment effect of active sites

Peinan He, Haisong Feng, Si Wang, Hu Ding, Yujie Liang, Min Ling and Xin Zhang*

*State Key Laboratory of Chemical Resource Engineering, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China*

***Corresponding author. E−mail: zhangxin@mail.buct.edu.cn**

# Contents

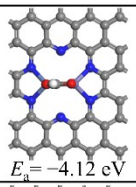
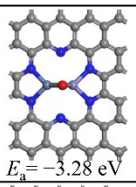
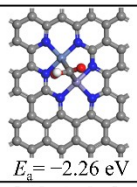
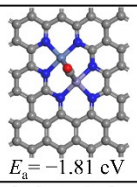
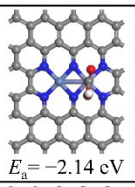
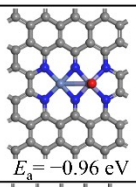
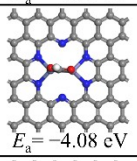
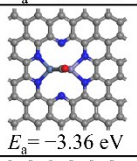
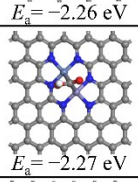
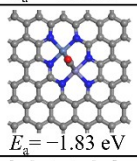
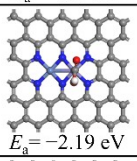
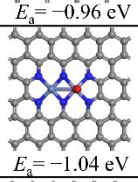
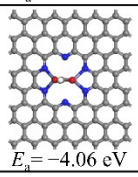
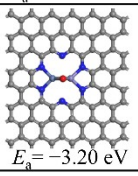
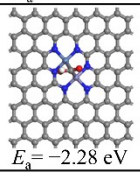
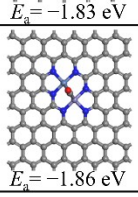
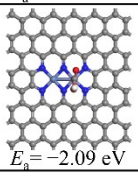
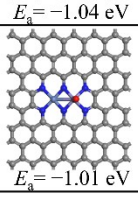
| | Model 1 | | Model 2 | | Model 3 | |
|---|---|---|---|---|---|---|
| **Surpercell** | *COOH | *CO | *COOH | *CO | *COOH | *CO |
| **4 × 3** |  $E_a$ = −4.12 eV |  $E_a$ = −3.28 eV |  $E_a$ = −2.26 eV |  $E_a$ = −1.81 eV |  $E_a$ = −2.14 eV |  $E_a$ = −0.96 eV |
| **5 × 3** |  $E_a$ = −4.08 eV |  $E_a$ = −3.36 eV |  $E_a$ = −2.27 eV |  $E_a$ = −1.83 eV |  $E_a$ = −2.19 eV |  $E_a$ = −1.04 eV |
| **6 × 4** |  $E_a$ = −4.06 eV |  $E_a$ = −3.20 eV |  $E_a$ = −2.28 eV |  $E_a$ = −1.86 eV |  $E_a$ = −2.09 eV |  $E_a$ = −1.01 eV |

**Fig. S1** The adsorption energies ($E_a$) of *COOH and *CO on 4 × 3, 5 × 3, and 6 × 4 supercells of Ni/Fe-$N_6$-Gra (Model 1, Model 2, Model 3) surfaces, respectively.

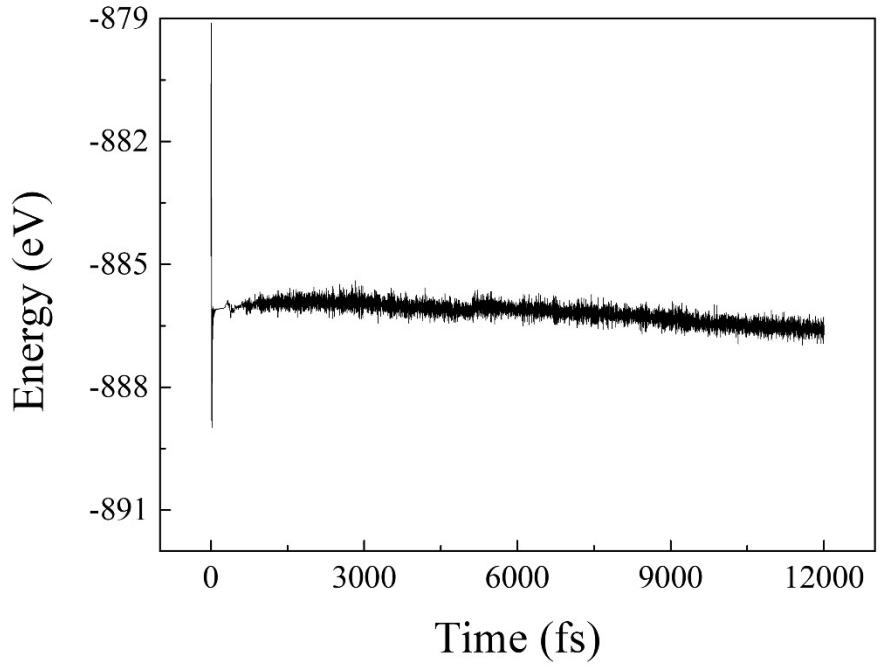



**Fig. S2** The AIMD simulation result of water/NiFe-$N_6$-Gra-Model 2 interface.

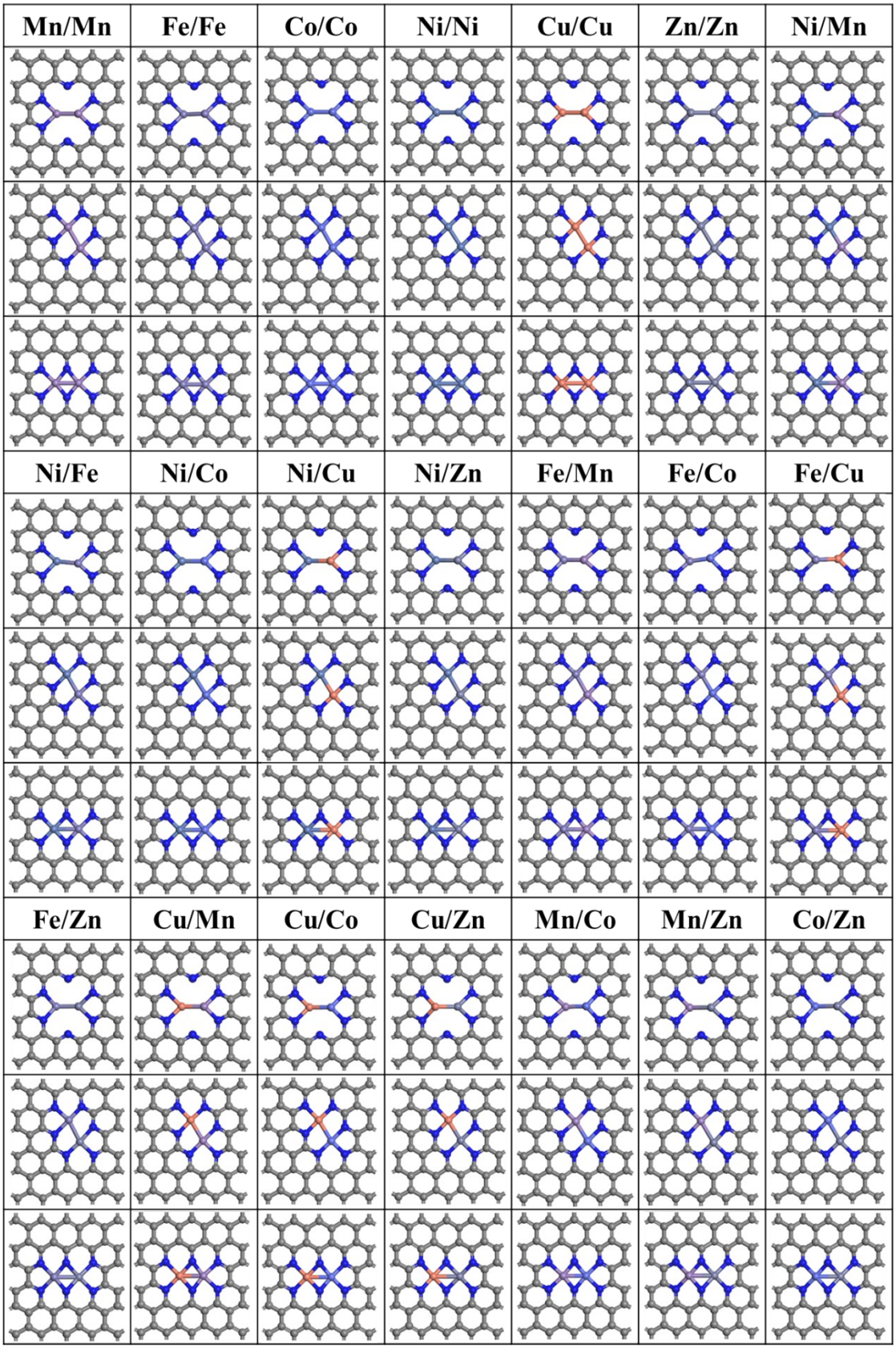



**Fig. S3** Optimized geometries of $M_1/M_2$-$N_6$-Gra substrate on Model 1, Model 2, and Model 3 (top view).

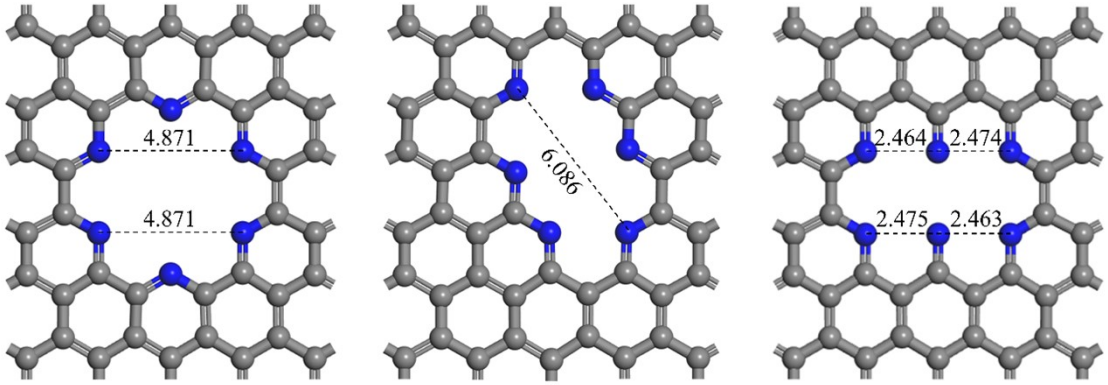



**Fig. S4** Optimized geometries of N-doped graphene substrate ($N_6$-Gra) on Model 1, Model 2, and Model 3. Unit is in Å.

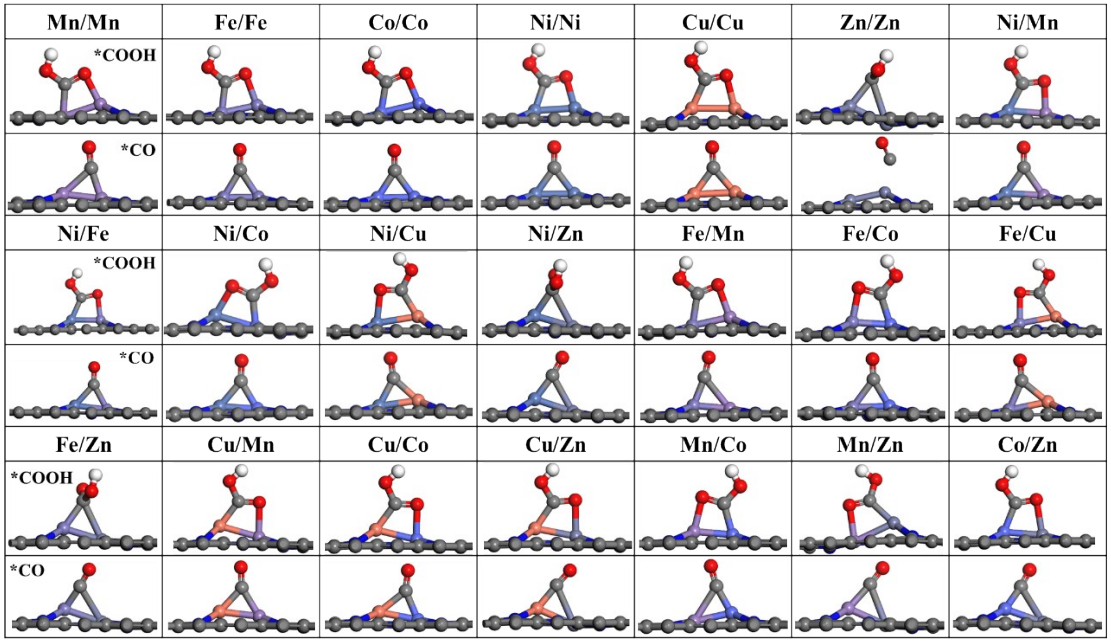



**Fig. S5** Optimized geometries of *COOH and *CO adsorbed $M_1/M_2$-$N_6$-Gra on Model 1 (side view).

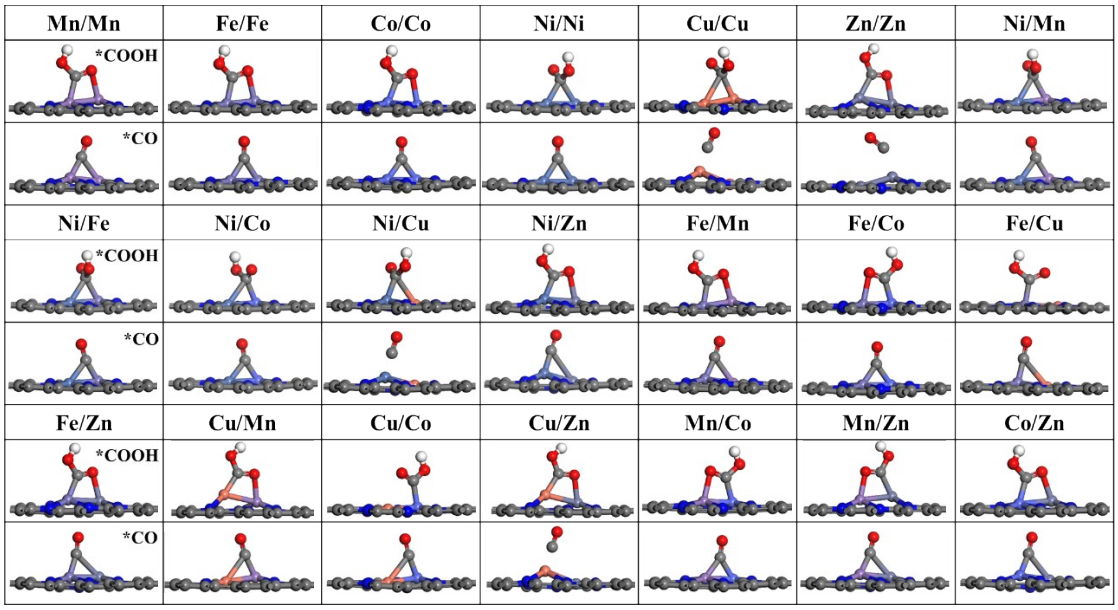



**Fig. S6** Optimized geometries of *COOH and *CO adsorbed $M_1/M_2$-$N_6$-Gra on Model 2 (side view).

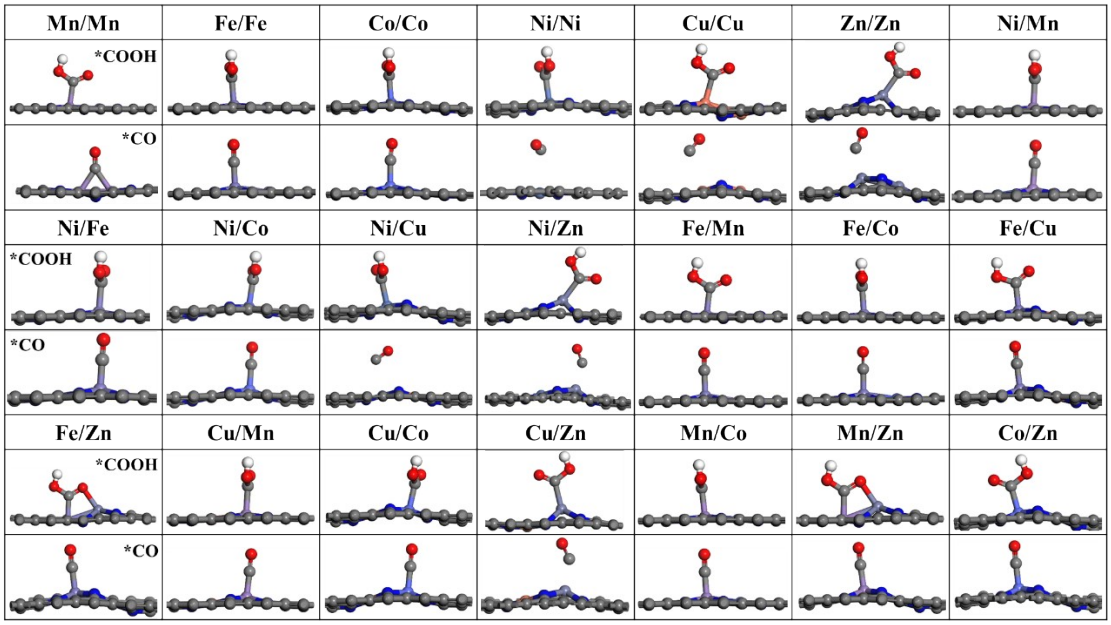



**Fig. S7** Optimized geometries of *COOH and *CO adsorbed $M_1/M_2$-$N_6$-Gra on Model 3 (side view).

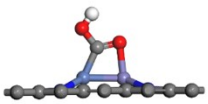
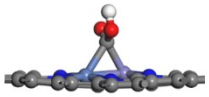
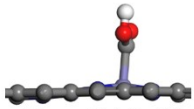
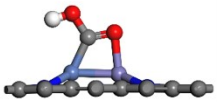
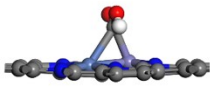
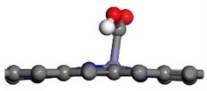
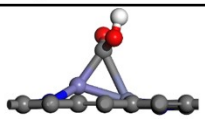
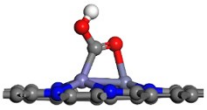
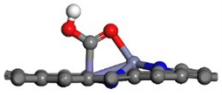
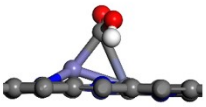
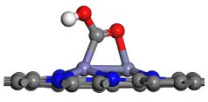
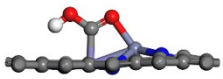
| | *COOH | Model 1 | Model 2 | Model 3 |
|---|---|---|---|---|
| **Ni/Fe-$N_6$-Gra** | H-up |  $E_a$ = −4.12 eV |  $E_a$ = −2.26 eV |  $E_a$ = −2.14 eV |
| | H-down |  $E_a$ = −4.00 eV |  $E_a$ = −1.77 eV |  $E_a$ = −2.06 eV |
| **Fe/Zn-$N_6$-Gra** | H-up |  $E_a$ = −2.97 eV |  $E_a$ = −3.08 eV |  $E_a$ = −2.35 eV |
| | H-down |  $E_a$ = −2.88 eV |  $E_a$ = −2.98 eV |  $E_a$ = −2.26 eV |

**Fig. S8** Optimized geometries and adsorption energies ($E_a$) of adsorbed cis-COOH (H-up) and trans-COOH (H-down) on Ni/Fe-$N_6$-Gra and Fe/Zn-$N_6$-Gra.

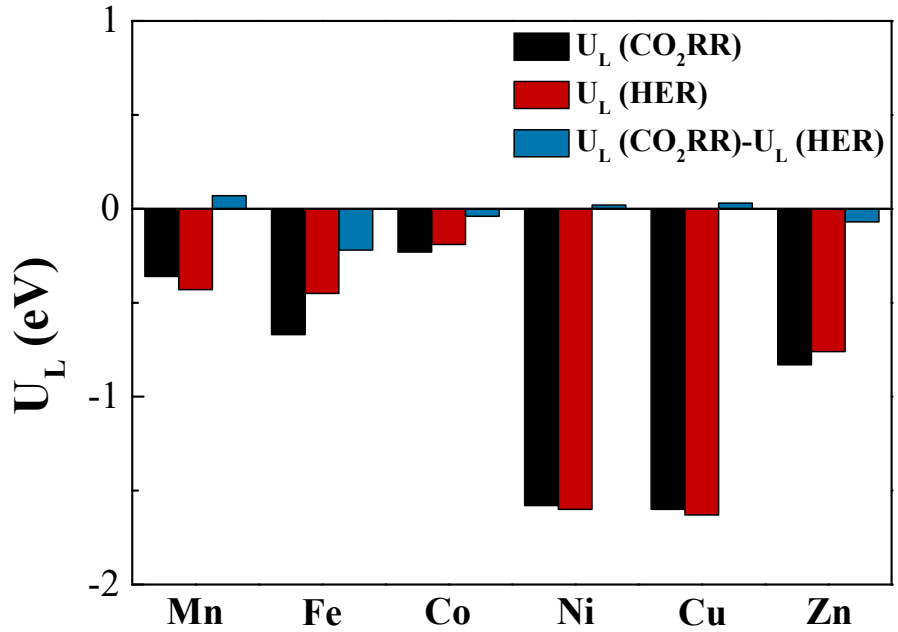



**Fig. S9** Calculated limiting potentials for HER ($U_L$(HER)), $CO_2$RR ($U_L$($CO_2$RR)), and ($U_L$($CO_2$RR) – $U_L$(HER)) on M-$N_4$-Gra (M = Mn, Fe, Co, Ni, Cu, and Zn).

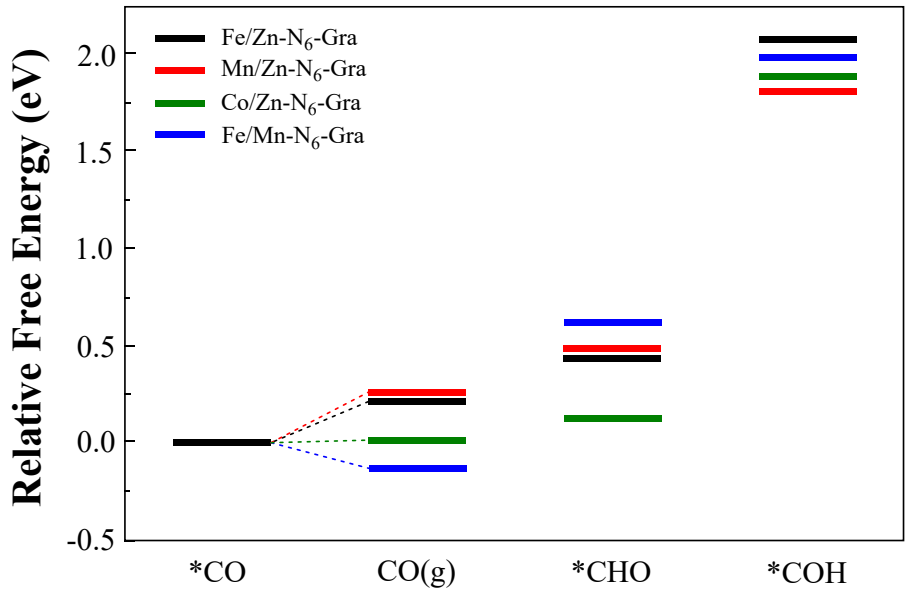



**Fig. S10** Relative free energy diagrams of the hydrogenation of CO to *CHO and *COH.

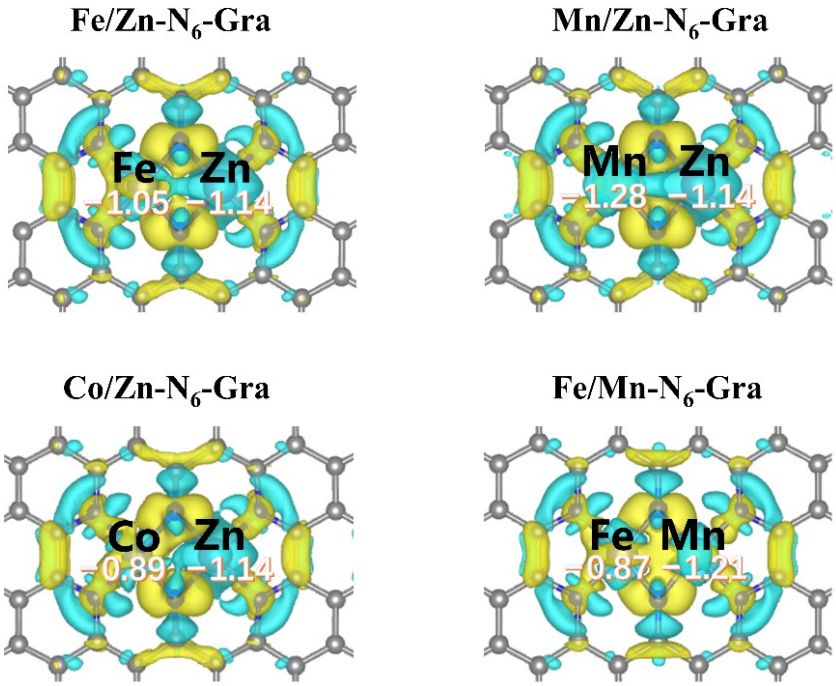



**Fig. S11** The charge density difference for Fe/Zn-$N_6$-Gra, Mn/Zn-$N_6$-Gra, Co/Zn-$N_6$-Gra, and Fe/Mn-$N_6$-Gra.Yellow: charge accumulation; Cyan: charge depletion. The isosurface value is set to 0.003 e/Bohr$^3$.

**Table S1.** The formation energies ($E_f$) on $M_1/M_2$-$N_6$-Gra.

| $M_1/M_2$-$N_6$-Gra | $E_f$(eV) | | |
|---|---|---|---|
| | Model 1 | Model 2 | Model 3 |
| Ni/Mn | 1.12 | −2.20 | −6.91 |
| Ni/Fe | 3.01 | −0.91 | −5.75 |
| Ni/Co | 2.09 | −1.27 | −5.94 |
| Ni/Ni | 1.70 | −1.93 | −6.03 |
| Ni/Cu | 1.60 | −1.39 | −4.58 |
| Ni/Zn | 0.56 | −1.86 | −5.22 |
| Fe/Mn | 1.98 | −0.70 | −7.27 |
| Fe/Fe | 2.83 | −0.02 | −6.19 |
| Fe/Co | 3.26 | −0.68 | −6.27 |
| Fe/Cu | 2.16 | −0.43 | −4.00 |
| Fe/Zn | 0.97 | −0.58 | −4.79 |
| Cu/Mn | 2.33 | −1.47 | −5.15 |
| Cu/Co | 2.11 | −0.98 | −4.27 |
| Cu/Cu | 1.65 | −4.90 | −3.40 |
| Cu/Zn | 0.42 | −1.90 | −4.07 |
| Mn/Mn | 1.11 | −1.42 | −8.12 |
| Mn/Co | 1.39 | −1.41 | −7.46 |
| Mn/Zn | 1.10 | −1.70 | −5.96 |
| Co/Co | 2.61 | −0.87 | −6.24 |
| Co/Zn | 0.88 | −1.21 | −4.89 |
| Zn/Zn | −1.47 | −2.22 | −4.58 |

**Table S2.** Bond lengths between bimetals on $M_1/M_2$-$N_6$-Gra.

| $M_1/M_2$-$N_6$-Gra | $d(M_1—M_2)$ (Å) | | |
|---|---|---|---|
| | Model 1 | Model 2 | Model 3 |
| Ni/Mn | 2.252 | 2.264 | 2.462 |
| Ni/Fe | 2.216 | 2.274 | 2.438 |
| Ni/Co | 2.247 | 2.307 | 2.423 |
| Ni/Ni | 2.342 | 2.341 | 2.580 |
| Ni/Cu | 2.298 | 2.381 | 2.547 |
| Ni/Zn | 2.294 | 2.425 | 2.546 |
| Fe/Mn | 2.134 | 2.337 | 2.236 |
| Fe/Fe | 2.281 | 2.208 | 2.221 |
| Fe/Co | 2.108 | 2.166 | 2.250 |
| Fe/Cu | 2.289 | 2.397 | 2.445 |
| Fe/Zn | 2.303 | 2.430 | 2.451 |
| Cu/Mn | 2.230 | 2.398 | 2.325 |
| Cu/Co | 2.290 | 2.395 | 2.428 |
| Cu/Cu | 2.329 | 2.382 | 2.576 |
| Cu/Zn | 2.241 | 2.386 | 2.632 |
| Mn/Mn | 2.217 | 2.372 | 2.266 |
| Mn/Co | 2.184 | 2.224 | 2.258 |
| Mn/Zn | 2.315 | 2.491 | 2.514 |
| Co/Co | 2.236 | 2.229 | 2.258 |
| Co/Zn | 2.310 | 2.408 | 2.470 |
| Zn/Zn | 2.221 | 2.546 | 2.553 |

**Table S3.** Free energy change values of elementary steps for $CO_2RR$ at $U$ = 0 V on $M_1/M_2$-$N_6$-Gra. Unit is in eV.

| $M_1/M_2$-$N_6$-Gra | Model 1 | | | Model 2 | | | Model 3 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\Delta G_1$ | $\Delta G_2$ | $\Delta G_3$ | $\Delta G_1$ | $\Delta G_2$ | $\Delta G_3$ | $\Delta G_1$ | $\Delta G_2$ | $\Delta G_3$ |
| Ni/Mn | −1.13 | −0.30 | 1.56 | 0.30 | −0.56 | 0.39 | 0.31 | −0.36 | 0.18 |
| Ni/Fe | −1.61 | −0.61 | 2.35 | 0.23 | −0.98 | 0.87 | 0.39 | −0.29 | 0.03 |
| Ni/Co | −0.47 | −1.13 | 1.73 | −0.08 | −0.81 | 1.02 | 0.54 | −0.08 | −0.33 |
| Ni/Ni | −0.19 | −1.33 | 1.65 | 0.62 | −0.58 | 0.09 | 1.47 | −0.66 | −0.68 |
| Ni/Cu | −0.23 | −1.10 | 1.46 | 0.73 | −0.58 | −0.03 | 1.49 | −0.63 | −0.73 |
| Ni/Zn | −0.73 | −0.87 | 1.73 | 0.09 | −0.55 | 0.59 | 1.06 | −0.34 | −0.59 |
| Fe/Mn | −1.20 | −0.29 | 1.62 | −0.65 | −0.68 | 1.46 | 0.26 | 0.01 | −0.14 |
| Fe/Fe | −0.82 | −0.55 | 1.50 | −0.32 | −0.77 | 1.22 | 0.48 | −0.06 | −0.29 |
| Fe/Co | −1.54 | −0.65 | 2.32 | 0.10 | −0.91 | 0.94 | 0.42 | 0.01 | −0.30 |
| Fe/Cu | −0.62 | −0.72 | 1.47 | 0.01 | −0.68 | 0.80 | 0.22 | −0.34 | 0.25 |
| Fe/Zn | −0.47 | −0.75 | 1.35 | −0.56 | −0.65 | 1.34 | 0.19 | −0.30 | 0.24 |
| Cu/Mn | −2.32 | −0.05 | 2.50 | 0.17 | −0.55 | 0.51 | 0.25 | −0.39 | 0.27 |
| Cu/Co | −0.57 | −0.97 | 1.67 | 0.13 | −0.64 | 0.64 | 0.42 | 0.04 | −0.33 |
| Cu/Cu | −0.33 | −0.97 | 1.43 | 1.09 | −0.79 | −0.17 | 1.83 | −0.98 | −0.72 |
| Cu/Zn | −0.59 | 0.07 | 0.65 | 0.40 | −0.19 | −0.08 | 0.86 | −0.10 | −0.63 |
| Mn/Mn | −0.81 | −0.38 | 1.32 | −0.57 | −0.75 | 1.45 | 0.08 | 0.32 | −0.27 |
| Mn/Co | −1.15 | −0.46 | 1.74 | −0.53 | −0.56 | 1.22 | 0.34 | −0.42 | 0.21 |
| Mn/Zn | −1.26 | −0.60 | 1.99 | −0.63 | −0.32 | 1.08 | 0.15 | −0.28 | 0.26 |
| Co/Co | −0.85 | −0.84 | 1.82 | 0.09 | −1.31 | 1.35 | 0.89 | 0.06 | −0.82 |
| Co/Zn | −0.55 | −0.99 | 1.67 | −0.45 | −0.62 | 1.20 | 0.20 | −0.09 | 0.02 |
| Zn/Zn | 0.81 | −0.18 | −0.50 | −0.50 | 1.08 | −0.45 | 1.01 | −0.37 | −0.51 |

Note: The red values represent the maximum free energy change values on the reaction pathway.

**Table S4.** Adsorption energies of *CO and *COOH on $M_1/M_2$-$N_6$-Gra. Unit is in eV.

| $M_1/M_2$-$N_6$-Gra | Model 1 | | Model2 | | Model 3 | |
|---|---|---|---|---|---|---|
| | $E_a$(*COOH) | $E_a$(*CO) | $E_a$(*COOH) | $E_a$(*CO) | $E_a$(*COOH) | $E_a$(*CO) |
| Ni/Mn | −3.65 | −2.49 | −2.17 | −1.34 | −2.18 | −1.11 |
| Ni/Fe | −4.12 | −3.28 | −2.26 | −1.81 | −2.14 | −0.96 |
| Ni/Co | −2.98 | −2.66 | −2.58 | −1.96 | −1.96 | −0.58 |
| Ni/Ni | −2.72 | −2.61 | −1.90 | −1.00 | −1.01 | −0.09 |
| Ni/Cu | −2.74 | −2.40 | −1.77 | −0.89 | −1.01 | −0.07 |
| Ni/Zn | −3.20 | −2.69 | −2.42 | −1.49 | −1.40 | −0.27 |
| Fe/Mn | −3.69 | −2.53 | −3.18 | −2.40 | −2.25 | −0.80 |
| Fe/Fe | −3.33 | −2.41 | −2.83 | −2.17 | −2.04 | −0.64 |
| Fe/Co | −4.06 | −3.25 | −2.45 | −1.89 | −2.09 | −0.64 |
| Fe/Cu | −3.13 | −2.39 | −2.47 | −1.76 | −2.28 | −1.18 |
| Fe/Zn | −2.97 | −2.27 | −3.08 | −2.28 | −2.35 | −1.17 |
| Cu/Mn | −4.86 | −3.46 | −2.34 | −1.42 | −2.25 | −1.20 |
| Cu/Co | −3.07 | −2.59 | −2.38 | −1.56 | −2.09 | −0.76 |
| Cu/Cu | −2.82 | −2.36 | −1.37 | −0.75 | −0.65 | −0.08 |
| Cu/Zn | −3.12 | −1.60 | −2.13 | −0.85 | −1.63 | −0.21 |
| Mn/Mn | −3.32 | −2.23 | −3.09 | −2.34 | −2.41 | −0.65 |
| Mn/Co | −3.65 | −2.66 | −3.09 | −2.16 | −2.16 | −1.15 |
| Mn/Zn | −3.75 | −2.93 | −3.13 | −2.00 | −2.39 | −1.86 |
| Co/Co | −3.35 | −2.75 | −2.45 | −2.30 | −1.61 | −0.11 |
| Co/Zn | −3.04 | −2.61 | −2.97 | −2.14 | −2.29 | −0.96 |
| Zn/Zn | −1.68 | −0.38 | −3.03 | −0.40 | −1.48 | −0.34 |

**Table S5.** Adsorption free energies of *CO and *COOH on $M_1/M_2$-$N_6$-Gra. Unit is in eV.

| $M_1/M_2$-$N_6$-Gra | Model 1 | | Model2 | | Model 3 | |
|---|---|---|---|---|---|---|
| | $\Delta G_{*COOH}$ | $\Delta G_{*CO}$ | $\Delta G_{*COOH}$ | $\Delta G_{*CO}$ | $\Delta G_{*COOH}$ | $\Delta G_{*CO}$ |
| Ni/Mn | −3.12 | −2.35 | −1.69 | −1.18 | −1.68 | −0.97 |
| Ni/Fe | −3.60 | −3.14 | −1.78 | −1.64 | −1.59 | −0.81 |
| Ni/Co | −2.46 | −2.52 | −2.07 | −1.81 | −1.46 | −0.45 |
| Ni/Ni | −2.18 | −2.44 | −1.38 | −0.88 | −0.52 | −0.11 |
| Ni/Cu | −2.23 | −2.25 | −1.27 | −0.77 | −0.50 | −0.06 |
| Ni/Zn | −2.73 | −2.52 | −1.90 | −1.38 | −0.70 | −0.18 |
| Fe/Mn | −3.19 | −2.41 | −2.64 | −2.25 | −1.74 | −0.65 |
| Fe/Fe | −2.81 | −2.29 | −2.31 | −2.01 | −1.52 | −0.50 |
| Fe/Co | −3.54 | −3.11 | −1.90 | −1.73 | −1.57 | −0.49 |
| Fe/Cu | −2.61 | −2.26 | −1.99 | −1.59 | −1.78 | −1.04 |
| Fe/Zn | −2.46 | −2.14 | −2.55 | −2.13 | −1.81 | −1.03 |
| Cu/Mn | −4.31 | −3.29 | −1.83 | −1.30 | −1.74 | −1.06 |
| Cu/Co | −2.56 | −2.46 | −1.86 | −1.43 | −1.58 | −0.46 |
| Cu/Cu | −2.32 | −2.22 | −0.91 | −0.62 | −0.17 | −0.07 |
| Cu/Zn | −2.58 | −1.44 | −1.60 | −0.71 | −1.13 | −0.17 |
| Mn/Mn | −2.81 | −2.11 | −2.56 | −2.24 | −1.92 | −0.52 |
| Mn/Co | −3.14 | −2.53 | −2.53 | −2.01 | −1.66 | −1.00 |
| Mn/Zn | −3.25 | −2.78 | −2.62 | −1.87 | −1.84 | −1.05 |
| Co/Co | −2.84 | −2.61 | −1.91 | −2.14 | −1.11 | 0.03 |
| Co/Zn | −2.55 | −2.46 | −2.44 | −1.99 | −1.79 | −0.81 |
| Zn/Zn | −1.18 | −0.28 | −2.50 | −0.34 | −0.99 | −0.28 |

**Table S6.** Bond lengths ($d(M_1—C)$ and $d(M_2—C)$) of *CO adsorbed $M_1/M_2$-$N_6$-Gra. Unit is in Å.

| $M_1/M_2$-$N_6$-Gra | Model 1 | | Model 2 | | Model 3 | |
|---|---|---|---|---|---|---|
| | $d(M_1—C)$ | $d(M_2—C)$ | $d(M_1—C)$ | $d(M_2—C)$ | $d(M_1—C)$ | $d(M_2—C)$ |
| Ni/Mn | 1.832 | 1.986 | 2.043 | 1.816 | — | 1.745 |
| Ni/Fe | 1.905 | 1.871 | 2.119 | 1.747 | — | 1.734 |
| Ni/Co | 1.901 | 1.835 | 1.992 | 1.766 | — | 1.739 |
| Ni/Ni | 1.852 | 1.852 | 1.929 | 1.924 | — | — |
| Ni/Cu | 1.810 | 1.911 | 1.771 | 2.829 | — | — |
| Ni/Zn | 1.701 | 2.378 | 1.736 | 2.745 | — | — |
| Fe/Mn | 1.752 | 2.313 | 1.728 | 2.318 | 1.725 | — |
| Fe/Fe | 1.891 | 1.912 | 1.879 | 1.879 | 1.726 | — |
| Fe/Co | 2.017 | 1.807 | 1.859 | 1.868 | 1.726 | — |
| Fe/Cu | 1.840 | 1.942 | 1.719 | 2.728 | 1.722 | — |
| Fe/Zn | 1.750 | 2.508 | 1.740 | 2.403 | 1.721 | — |
| Cu/Mn | 1.907 | 1.935 | 2.404 | 1.804 | — | 1.747 |
| Cu/Co | 1.962 | 1.787 | 2.512 | 1.748 | — | 1.740 |
| Cu/Cu | 1.855 | 1.862 | — | — | — | — |
| Cu/Zn | 1.777 | 2.528 | — | — | — | — |
| Mn/Mn | 2.173 | 1.801 | 1.785 | 2.158 | 1.973 | 1.973 |
| Mn/Co | 2.350 | 1.736 | 1.938 | 1.845 | 1.749 | — |
| Mn/Zn | 1.865 | 2.489 | 1.795 | 2.294 | 1.765 | — |
| Co/Co | 1.858 | 1.886 | 1.846 | 1.848 | 1.818 | — |
| Co/Zn | 1.719 | 2.472 | 1.725 | 2.442 | 1.731 | — |
| Zn/Zn | — | — | — | — | — | — |

**Table S7.** Bond lengths of *COOH adsorbed $M_1/M_2$-$N_6$-Gra on Model 1, Model 2, and Model 3. Unit is in Å.

| Model 1 | $d(M_1—C)$ | $d(M_1—O)$ | $d(M_2—C)$ | $d(M_2—O)$ |
|---|---|---|---|---|
| Ni/Mn | 1.829 | — | — | 1.920 |
| Ni/Fe | 1.854 | — | — | 2.007 |
| Ni/Co | — | 1.927 | 1.797 | — |
| Ni/Ni | 1.821 | — | — | 1.955 |
| Ni/Cu | — | 2.022 | 1.871 | — |
| Ni/Zn | 1.888 | — | 2.434 | — |
| Fe/Mn | 1.870 | — | — | 1.990 |
| Fe/Fe | 1.832 | — | — | 1.983 |
| Fe/Co | — | 1.982 | 1.853 | — |
| Fe/Cu | — | 2.045 | 1.880 | — |
| Fe/Zn | 1.951 | — | 2.484 | — |
| Cu/Mn | 1.871 | — | — | 2.101 |
| Cu/Co | 1.879 | — | — | 2.042 |
| Cu/Cu | 1.870 | — | — | 2.001 |
| Cu/Zn | 1.878 | — | — | 2.105 |
| Mn/Mn | 1.870 | — | 1.986 | — |
| Mn/Co | — | 2.004 | 1.836 | — |
| Mn/Zn | — | 2.198 | 1.968 | — |
| Co/Co | 1.853 | — | — | 1.957 |
| Co/Zn | 1.872 | — | — | 2.151 |
| Zn/Zn | 2.025 | — | 2.733 | — |

| Model 2 | $d(M_1—C)$ | $d(M_1—O)$ | $d(M_2—C)$ | $d(M_2—O)$ |
|---|---|---|---|---|
| Ni/Mn | 2.261 | — | 2.006 | — |
| Ni/Fe | 2.189 | — | 1.952 | — |
| Ni/Co | 2.365 | — | 1.909 | — |
| Ni/Ni | 2.046 | — | 2.070 | — |
| Ni/Cu | 1.941 | — | 2.515 | — |
| Ni/Zn | 1.877 | — | — | 2.139 |
| Fe/Mn | 1.840 | — | — | 2.078 |
| Fe/Fe | 1.854 | — | — | 2.014 |
| Fe/Co | — | 2.260 | 1.857 | — |
| Fe/Cu | 1.864 | — | — | — |
| Fe/Zn | 1.916 | — | — | 2.070 |
| Cu/Mn | 1.869 | — | — | 2.052 |
| Cu/Co | — | — | 1.862 | — |

| | | | | |
|---|---|---|---|---|
| Cu/Cu | 2.009 | — | 2.575 | — |
| Cu/Zn | 1.881 | — | — | 2.044 |
| Mn/Mn | 1.924 | — | — | 2.106 |
| Mn/Co | — | 2.181 | 1.845 | — |
| Mn/Zn | — | 2.119 | 2.020 | — |
| Co/Co | 1.855 | — | — | 2.152 |
| Co/Zn | 1.854 | — | — | 2.084 |
| Zn/Zn | 2.003 | — | — | 2.098 |

| Model 3 | $d(M_1—C)$ | $d(M_1—O)$ | $d(M_2—C)$ | $d(M_2—O)$ |
|---|---|---|---|---|
| Ni/Mn | — | — | 1.947 | — |
| Ni/Fe | — | — | 1.923 | — |
| Ni/Co | — | — | 1.897 | — |
| Ni/Ni | 1.963 | — | — | — |
| Ni/Cu | 1.952 | — | — | — |
| Ni/Zn | — | — | 2.019 | — |
| Fe/Mn | 1.882 | — | — | — |
| Fe/Fe | 1.920 | — | — | — |
| Fe/Co | 1.914 | — | — | — |
| Fe/Cu | 1.918 | — | — | — |
| Fe/Zn | 1.880 | — | — | 2.091 |
| Cu/Mn | — | — | — | 1.951 |
| Cu/Co | — | — | — | 1.894 |
| Cu/Cu | 2.028 | — | — | — |
| Cu/Zn | — | — | — | 2.071 |
| Mn/Mn | 1.950 | — | — | — |
| Mn/Co | 1.960 | — | — | — |
| Mn/Zn | 1.917 | — | — | 2.065 |
| Co/Co | 1.912 | — | — | — |
| Co/Zn | 1.886 | — | — | — |
| Zn/Zn | 2.020 | — | — | — |

**Table S8.** The limiting potentials of HER at $U$ = 0 V on Model 2, and Model 3. Unit is in V.

| $M_1/M_2$-$N_6$-Gra | Model 2 | Model 3 |
|---|---|---|
| Ni/Mn | −0.14 | −0.31 |
| Ni/Fe | −0.08 | −0.33 |
| Ni/Co | −0.35 | −0.50 |
| Ni/Ni | −0.10 | −1.37 |
| Ni/Cu | −0.41 | −1.37 |
| Ni/Zn | −0.16 | −1.15 |
| Fe/Mn | −0.61 | −0.29 |
| Fe/Fe | −0.40 | −0.41 |
| Fe/Co | −0.10 | −0.37 |
| Fe/Cu | −0.17 | −0.20 |
| Fe/Zn | −0.67 | −0.32 |
| Cu/Mn | −0.07 | −0.22 |
| Cu/Co | −0.16 | −0.37 |
| Cu/Cu | −0.77 | −1.94 |
| Cu/Zn | −0.25 | −0.76 |
| Mn/Mn | −0.71 | −0.05 |
| Mn/Co | −0.54 | −0.31 |
| Mn/Zn | −0.59 | −0.33 |
| Co/Co | −0.21 | −0.82 |
| Co/Zn | −0.50 | −0.25 |
| Zn/Zn | −0.61 | −1.00 |

**Table S9.** The *d*-band center ($\varepsilon_d$) of $M_1/M_2$-$N_6$-Gra-Model 3. Unit is in eV.

| $M_1/M_2$-$N_6$-Gra | $\varepsilon_d$ ($M_1$) | $\varepsilon_d$ ($M_2$) |
|---|---|---|
| Mn/Mn | −0.74 | −0.74 |
| Fe/Fe | −1.53 | −1.52 |
| Co/Co | −1.96 | −1.97 |
| Ni/Ni | −1.93 | −1.94 |
| Cu/Cu | −3.37 | −3.37 |
| Zn/Zn | −5.86 | −5.87 |
| Ni/Mn | −2.00 | −0.86 |
| Ni/Fe | −2.22 | −1.49 |
| Ni/Co | −2.38 | −1.67 |
| Ni/Cu | −1.86 | −3.69 |
| Ni/Zn | −1.33 | −5.88 |
| Fe/Mn | −1.42 | −0.95 |
| Fe/Co | −1.33 | −1.80 |
| Fe/Cu | −1.53 | −3.53 |
| Fe/Zn | −1.55 | −6.34 |
| Cu/Mn | −3.68 | −1.07 |
| Cu/Co | −3.44 | −1.38 |
| Cu/Zn | −3.78 | −6.28 |
| Mn/Co | −1.27 | −1.75 |
| Mn/Zn | −0.76 | −6.18 |
| Co/Zn | −1.18 | −6.07 |

**Table S10.** The adsorption energies of intermediates, free energy change values of elementary steps and limiting potentials of Fe/Zn-$N_6$-Gra-Model 3 and Co/Zn-$N_6$-Gra-Model 3 at different U values and Cu/Fe-$N_6$-Gra-Model 2 at U = 4 eV. Unit is in eV.

| | U value | $E_a$(*COOH) | $E_a$(*CO) | $\Delta G_1$ | $\Delta G_2$ | $\Delta G_3$ | $U_L$ (V) |
|---|---|---|---|---|---|---|---|
| Fe/Zn-Model 3 | U = 3 | −1.70 | −0.45 | 0.85 | −0.28 | −0.44 | −0.85 |
| | U = 4 | −1.54 | −0.32 | 1.00 | −0.25 | −0.61 | −1.00 |
| | U = 5 | −1.09 | −0.27 | 1.45 | −0.73 | −0.59 | −1.45 |
| | U = 6 | −0.91 | −0.36 | 1.61 | −0.97 | −0.50 | −1.61 |
| Co/Zn-Model 3 | U = 3 | −2.29 | −0.96 | 0.44 | −0.14 | −0.17 | −0.44 |
| | U = 4 | −2.05 | −0.72 | 0.61 | −0.23 | −0.25 | −0.61 |
| | U = 5 | −1.90 | −0.64 | 0.81 | −0.35 | −0.34 | −0.81 |
| | U = 6 | −1.69 | −0.54 | 1.01 | −0.46 | −0.43 | −1.01 |
| Cu/Fe-Model 2 | U = 4 | −1.40 | −0.80 | 1.08 | −0.84 | −0.11 | −1.08 |

**Table S11.** Magnetic moments of metal atoms at different U values on Fe/Zn and Co/Zn-$N_6$-Gra-Model 3 Unit is in $\mu_B$.

| U value | Fe/Zn | | Co/Zn | |
|---|---|---|---|---|
| | mag($M_1$) | mag($M_2$) | mag($M_1$) | mag($M_2$) |
| U = 3 | 2.625 | 0.011 | −1.123 | 0.077 |
| U = 4 | 2.724 | 0.015 | −1.060 | 0.002 |
| U = 5 | 2.992 | 0.001 | −1.089 | 0.001 |
| U = 6 | 3.198 | 0.002 | −1.733 | 0.001 |