## Synergistic interaction between $g-C_3N_4$ and Cu-Zn-MOFs via electrostatic assembly for enhanced electrocatalytic CO<sub>2</sub> reduction

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Fig. S1. SEM and corresponding high-magnification images of ZIF-8.



Fig. S2. XRD patterns of ZIF-8 powder and ZIF-8 simulation.



Fig. S3. The crystal pattern of simulated ZIF-8.



**Fig. S4.** XPS survey spectrum of  $g-C_3N_4$ .



Fig. S5. XPS survey spectrum of Cu-Zn-MOFs.



Fig. S6. XPS survey spectrum of g-C<sub>3</sub>N<sub>4</sub>@Cu-Zn-MOFs-1:1.



Fig. S7. XPS spectrum. C 1s of g-C<sub>3</sub>N<sub>4</sub>.



Fig. S8. Potential-dependent Faradaic efficiency of (a)  $g-C_3N_4@Cu-Zn-MOFs-0.5:1$ , (b)  $g-C_3N_4@Cu-Zn-MOFs-0.75:1$ , (c)  $g-C_3N_4@Cu-Zn-MOFs-1.25:1$ , and (d)  $g-C_3N_4@Cu-Zn-MOFs-1.5:1$ .



Fig. S9. (a) TEM, (b) HRTEM, and (c) SAED images of  $g-C_3N_4@CuZn-MOFs-1:1$  after  $eCO_2R$ .



Fig. S10. Cyclic voltammograms of (a)  $g-C_3N_4$ @Cu-Zn-MOFs-1:1, (b)  $g-C_3N_4$ , and (c) Cu-Zn-MOFs at different scan rates.



Fig. S11. Zeta potential distribution of  $g-C_3N_4$ .



Fig. S12. Zeta potential distribution of Cu-Zn-MOFs.



Fig. S13. Zeta potential distribution of  $g-C_3N_4$ @Cu-Zn-MOFs-1:1.

**Table S1.** The contents of C, N, O, Zn, and Cu in  $g-C_3N_4$  (@Cu-Zn-MOFs-1:1 measured by the energy dispersive spectrometer (EDS) spectrum.

Elements	С	N	0	Zn	Cu
wt.%	64.44	21.19	7.08	6.44	0.86

Electrocatalysts	Potentials (V vs. RHE)	FE <sub>CO</sub> (%)	<i>jco</i> (mA cm <sup>-2</sup> )	References
g-C <sub>3</sub> N <sub>4</sub> @Cu-Zn- MOFs-1:1	-1.3	85	21.3	This work
Fe-N <sub>5</sub> /C	-0.7	67.8	3.8	[S1]
Fe NP/NC	-0.7	35.7	1.1	[S1]
g-C <sub>3</sub> N <sub>4</sub> /MWCNTs	-0.75	60	0.55	[S2]
CuSe/g-C <sub>3</sub> N <sub>4</sub>	-1.2	85.2	8.5	[S3]
NRMC-900	-0.7	80	2.9	[S4]
NCNTs	-0.8	80	0.8	[S5]
NC-900	-0.95	78	0.8	[S6]
ACN-850	-1.1	80	2.4	[S7]
$Ag/g-C_3N_4$	-0.7	94	10.1	[S8]
P-Ag/g-C <sub>3</sub> N <sub>4</sub>	-0.9	80.9	9.8	[S8]
PcCu-O <sub>8</sub> -Zn/CNT	-0.7	88	8	[S9]
Ag@Ui-66-SH	-1.1	74	19.5	[S10]
NiSA-N <sub>2</sub> -C	-0.8	98	14.7	[S11]
Cu-MOFs [Cu(L)SO <sub>4</sub> ]·H <sub>2</sub> O	-0.89	77.5	3	[812]
Ag <sub>2</sub> O/layered ZIF	-1.2	80.6	26.2	[S13]
Re-SURMOFs	-1.6	93	2.5	[S14]
2D Ni(Im) <sub>2</sub> -5 nm	-0.9	79.3	5.2	[S15]

**Table S2.** Summary of the reported NC-,  $g-C_3N_4$ -, and MOFs-based electrocatalysts for  $eCO_2R$  to CO.

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