Supporting Information

Synergistic effect of Cu and Fe small nanoparticles supported on porous N-doped graphitic frameworks for selective electrochemical CO_2 reduction at low overpotentials

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Table S1. List of samples under study and amounts of the Cu and Fe salts used in the preparation procedure.

Sample No.	$m_{Cu(OAC)2}$ (mg)	C_{FeCl2} (mg)
Cu@NG	75.03	-
CuFe@NG	37.52	29.79
CuFe2@NG	18.76	44.67
CuFe7@NG	9.38	52.13
Fe@NG	-	59.58

Table S2. Summary of the main activity performance of different electrocatalysts.

electrocatalyst	CO FE (%)	Potential (V vs. RHE)	Reference
CuFe2@NG	96	-0.3	This work
FeN_5/N-doped G	97	-0.6	1
Fe-N-C	90	-0.13 to -0.31	2
Fe/NC(N_2)	66	-0.5	3
Fe-N-C	80	-0.5	4
Cu-APC	92	-0.78	5
Fe@NBCT	98	-0.7	6
CuFe	95.5	-0.4	7

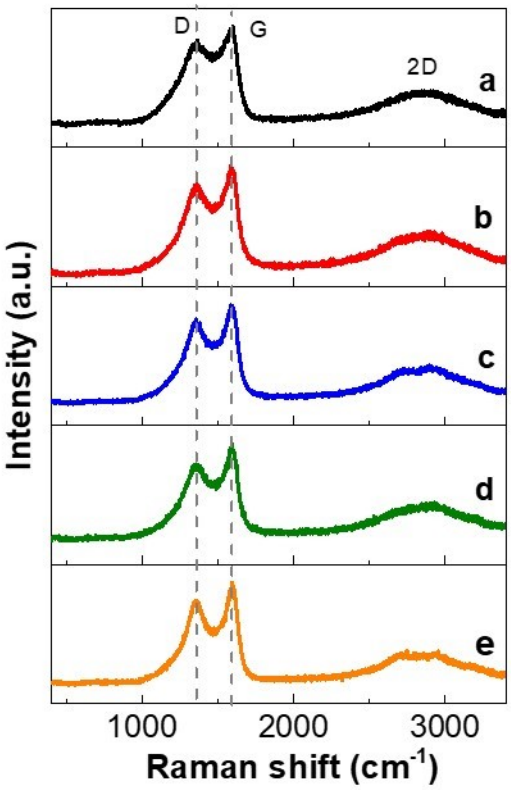

Figure S1. Raman spectra of Cu@NG (a), CuFe@NG (b), CuFe2@NG (c), CuFe7@NG (d) and Fe@NG (e). D and G band are indicated with dashed lines. Laser excitation 514 nm.

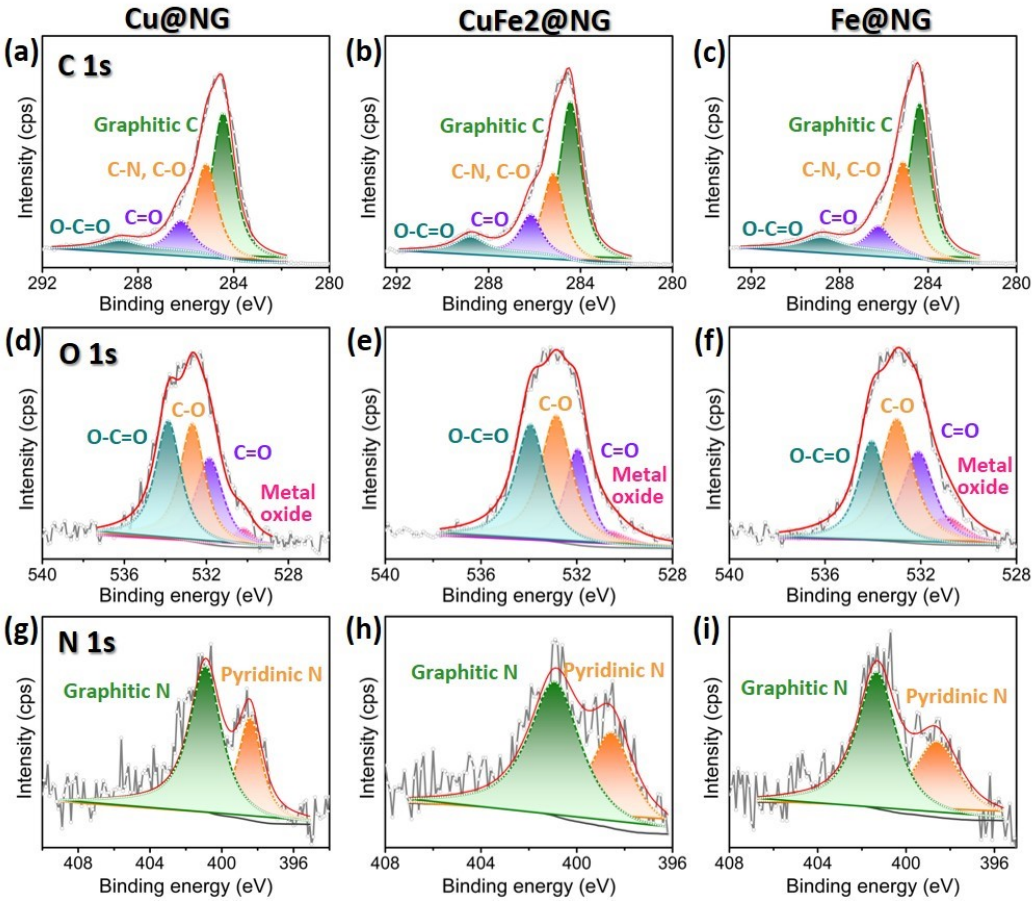

Figure S2. XPS C 1s, O 1s and N 1s spectra of Cu@NG (a,d,g), CuFe2@NG (b,e,h) and Fe@NG (c,f,i).

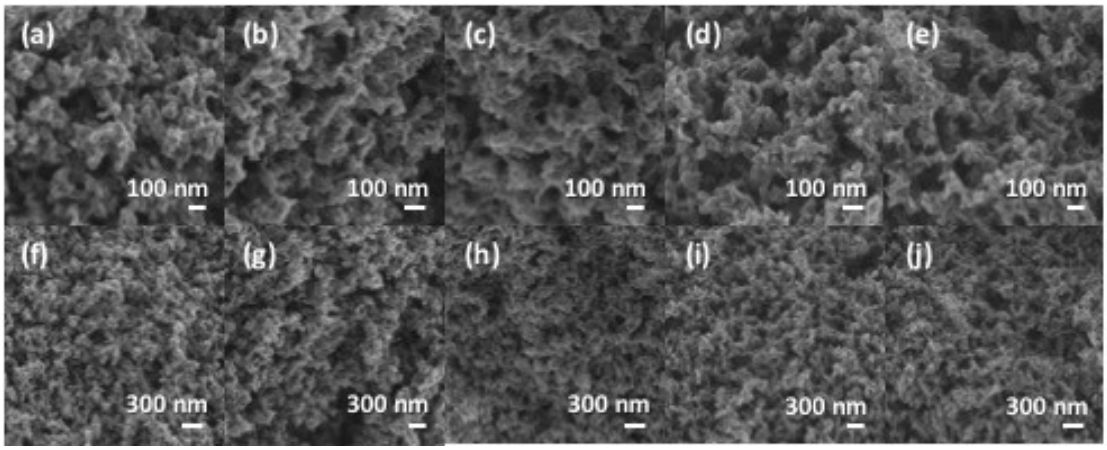

Figure S3. HR-FESEM images at two magnification of Cu@NG (a,f), CuFe@NG (b,g), CuFe2@NG (c,h), CuFe7NG (d,i) and Fe@NG (e,j).

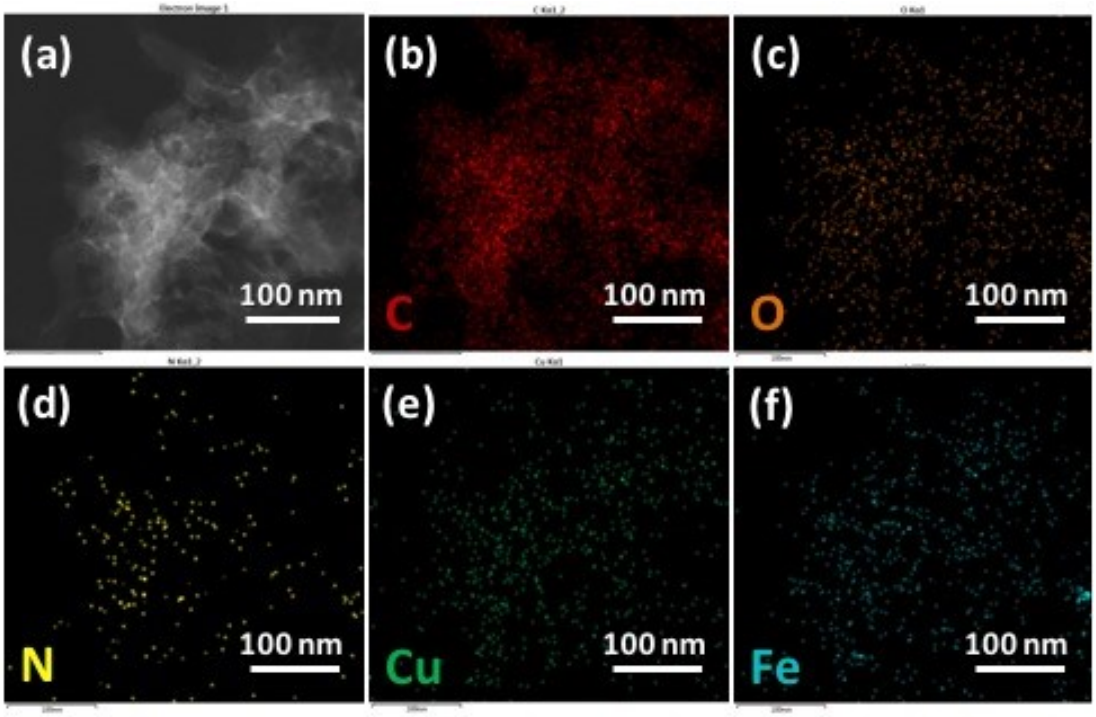

Figure S4. HADF-STEM image of CuFe2@NG (a) and elemental mapping (b-f).

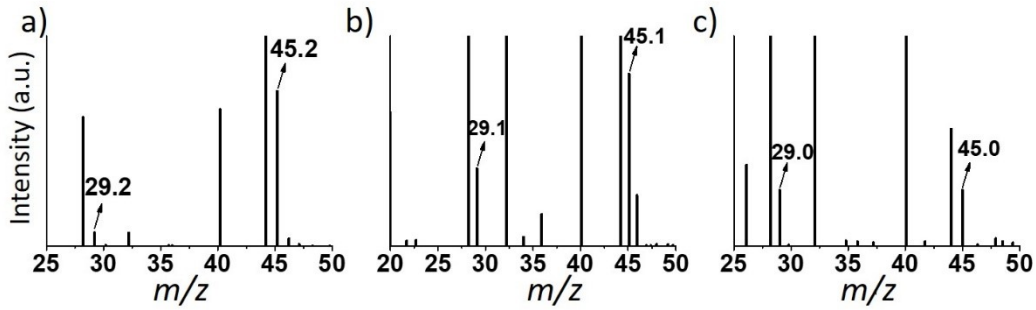

Figure S5. Mass spectra of the gas phase reaction products from $^{13}CO_2$ using CuFe2@NG at 0.5 (a), 1 (b) and 2 (c) h, showing that ^{13}CO is the main reaction product and the $^{13}CO/^{13}CO_2$ ratio grow with time, as revealed by the peak at *m/z* 29. The peaks at m/z 28, 32 and 40 correspond to N_2, O_2 and Ar, respectively. The peak at m/z 44 should correspond to unlabelled CO_2 coming from the $KHCO_3$ electrolyte.

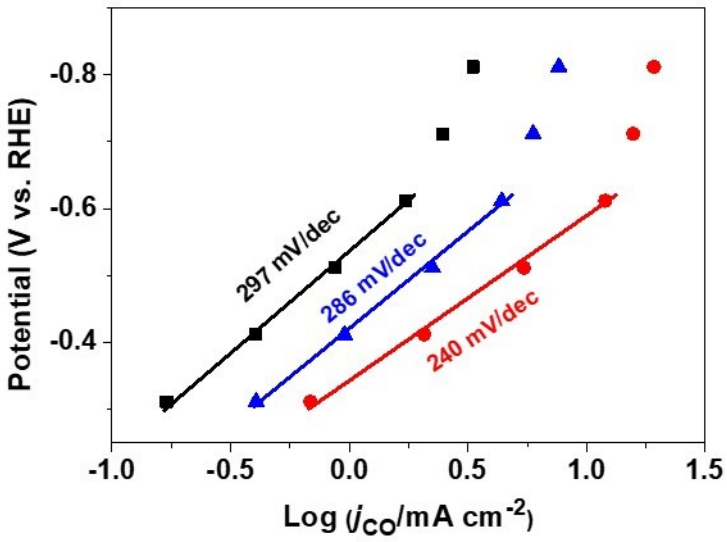

Figure S6. Tafel slopes calculated using Cu@NG (black squares), Fe@NG (blue triangles) and CuFe2@NG (red dots) as cathodes, Pt foil as anode, and Ag/AgCl $KCl_{Sat.}$ as reference electrode.

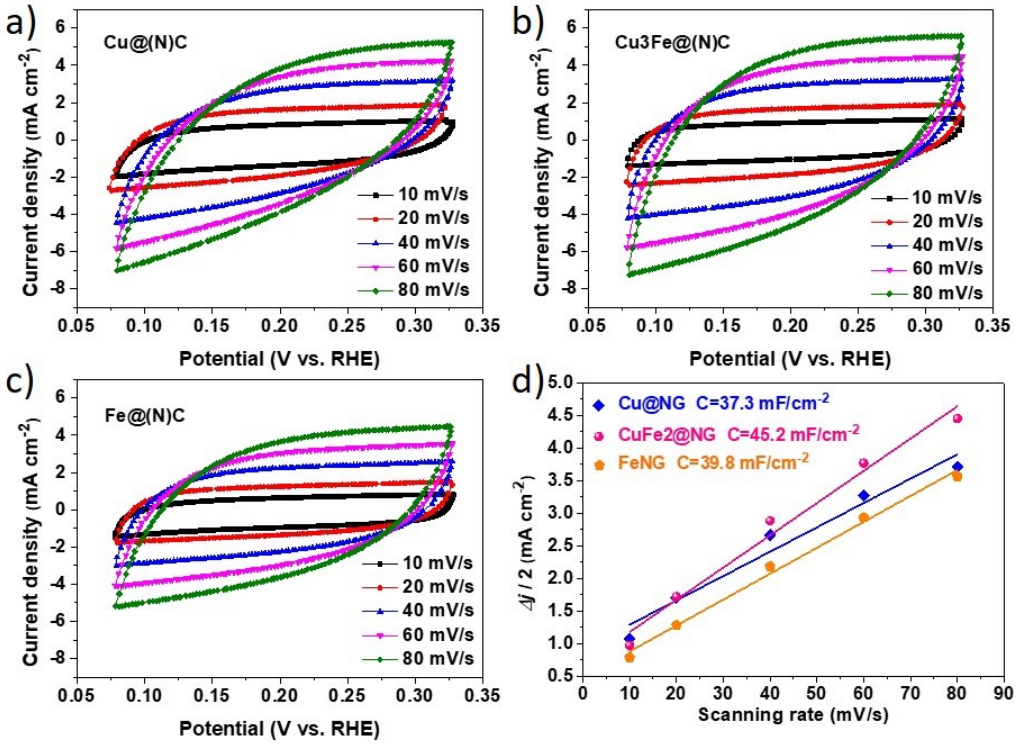

Figure S7. CV of Cu@NG (a), CuFe2@NG (b) and Fe@NG (c) at different scan rates measured in CO_2-saturated 1 M $KHCO_3$. (d) Capacitive currents of the samples as function of the scan rate.

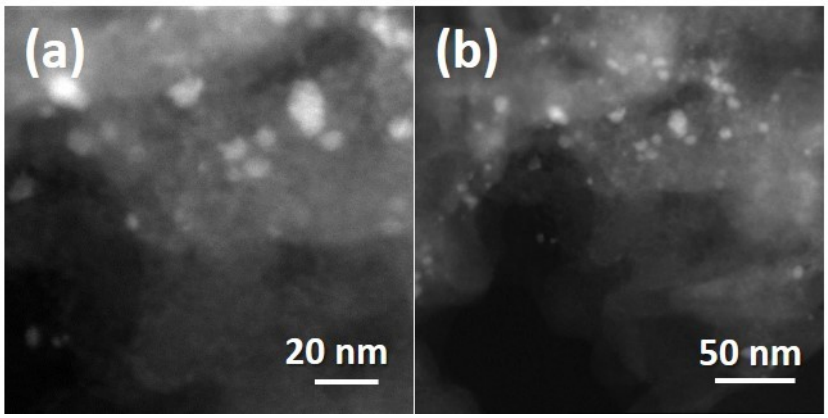

Figure S8. HADF-STEM images of CuFe2@NG after 17 h electrocatalytic test.

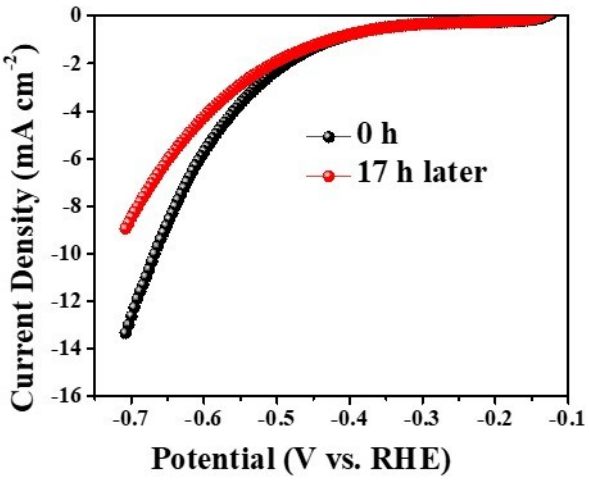

Figure S9. LSV curves acquired in Ar-saturated 1 M $KHCO_3$ solution before (black) and after (red) applied voltage of -0. 51 V vs. NHE for 17 h using CuFe2@NG and Pt wire as cathode and anode, respectively.

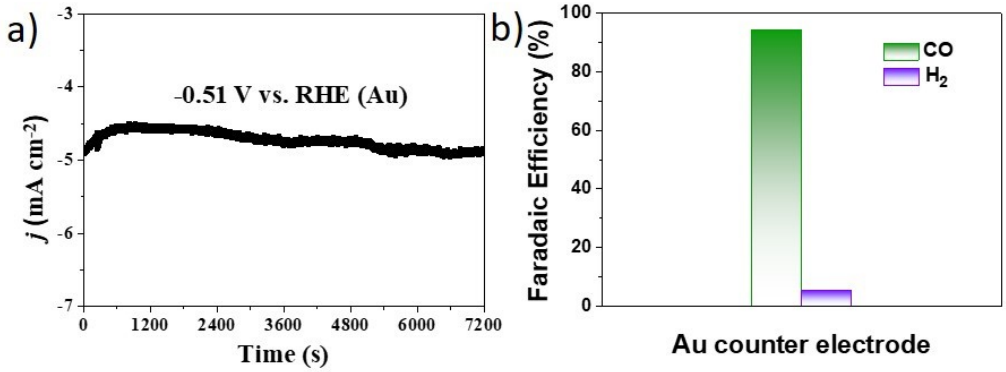

Figure S10. (a) Chronoamperometry and (b) faradaic efficiency of CuFe2@NC sample in CO_2-saturated 1M $KHCO_3$ solution using Au wire as counter electrode.

References

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