Supplementary Information (SI) for Journal of Materials Chemistry A.

Shielding effect in the synthesis of Gd-doped copper oxide catalysts with enhanced CO_2 electroreduction to ethylene

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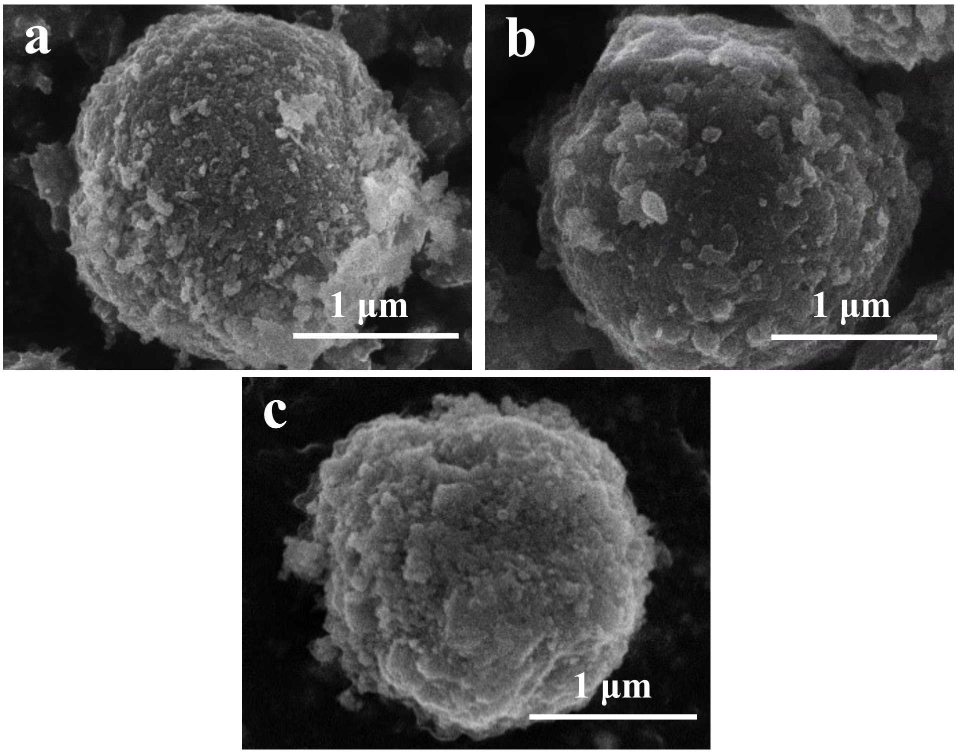


Figure S1. SEM images of Gd-CuO-W (a), Gd-CuO-M (b) and Gd-CuO-P (c).

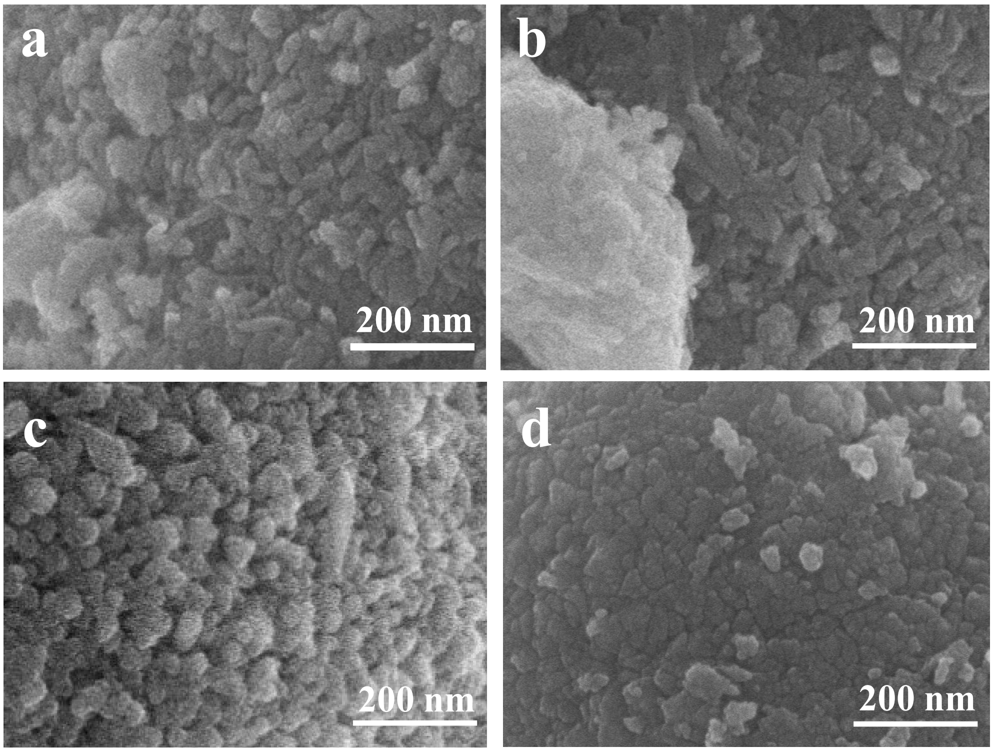


Figure S2. SEM images (a-d) of Gd-CuO-W, Gd-CuO-M, Gd-CuO-E and Gd-CuO-P.

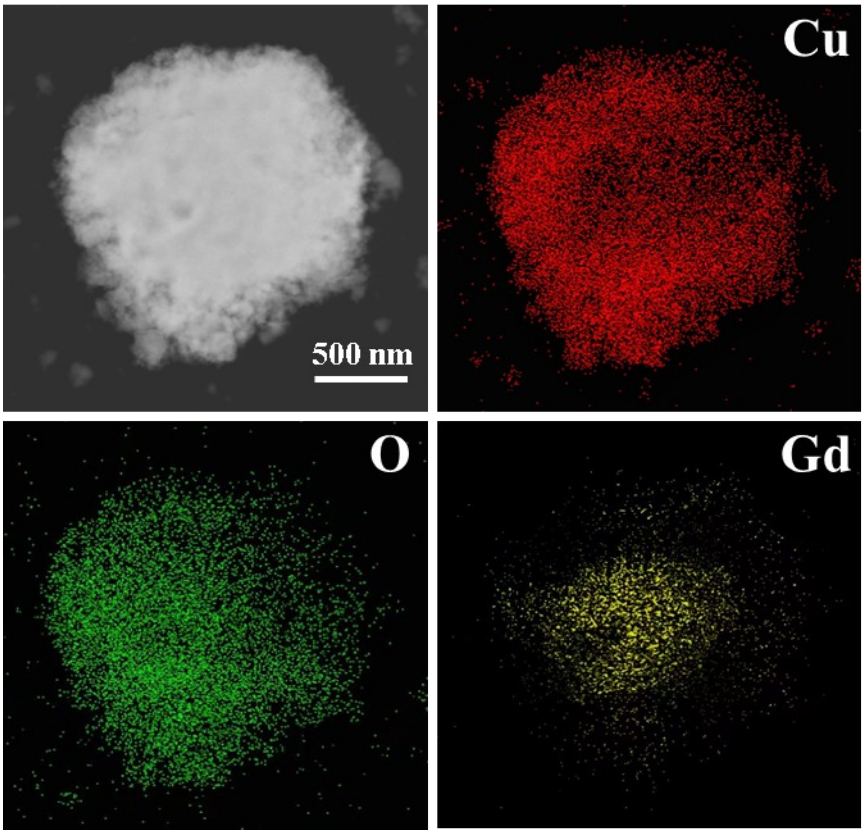


Figure S3. TEM-EDS-mapping of Gd-CuO-E.

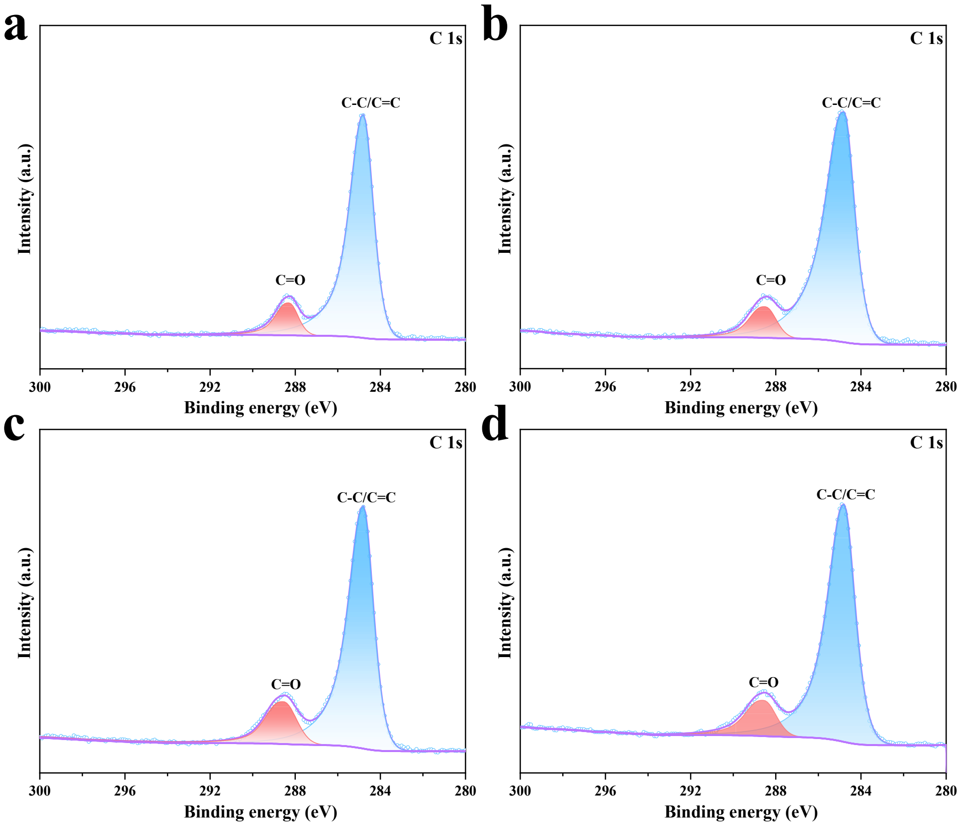


Figure S4. C 1s XPS spectra of Gd-CuO-W (a), Gd-CuO-M (b), Gd-CuO-E (c), and Gd-CuO-P (d).

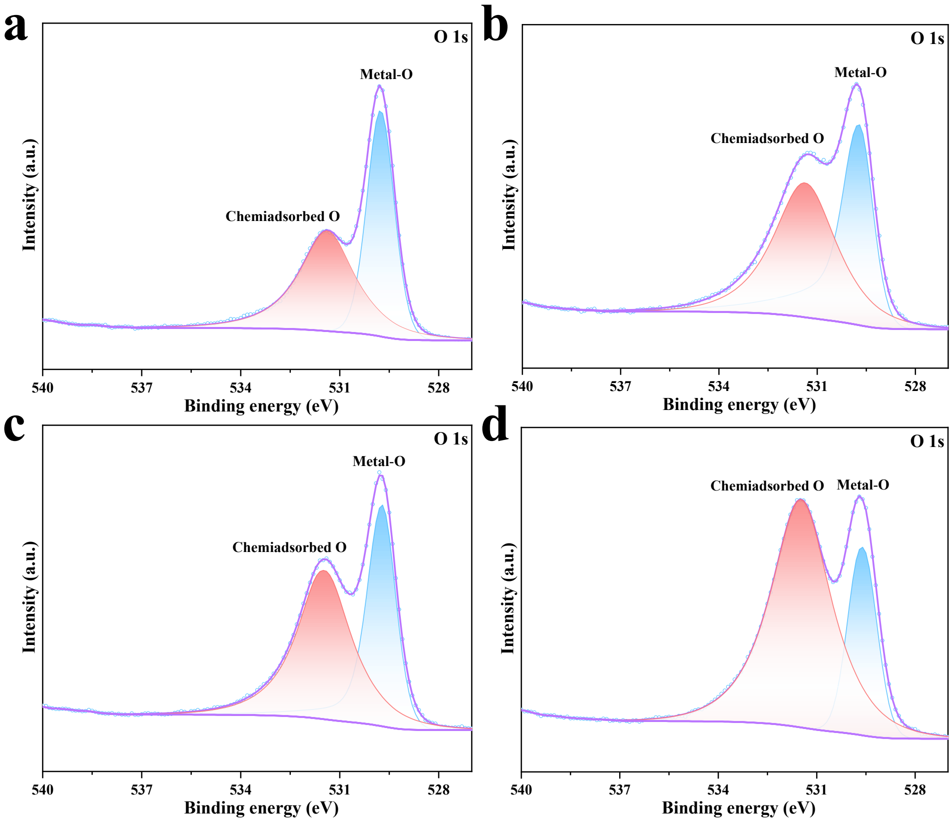


Figure S5. O 1s XPS spectra of Gd-CuO-W (a), Gd-CuO-M (b), Gd-CuO-E (c), and Gd-CuO-P (d).

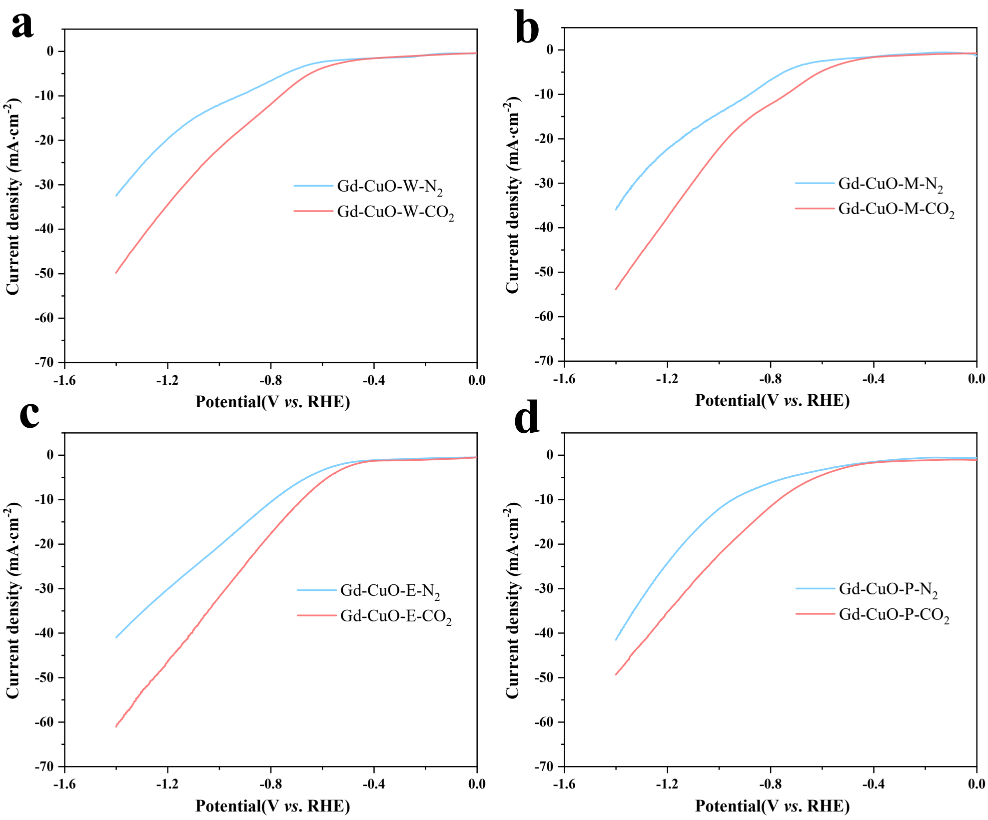


Figure S6. LSV curves of Gd-CuO-W(a), Gd-CuO-M(b), Gd-CuO-E(c), and Gd-CuO-P(d) catalysts in CO_2-or N_2-saturated 0.5 M $KHCO_3$ electrolyte in an H-cell.

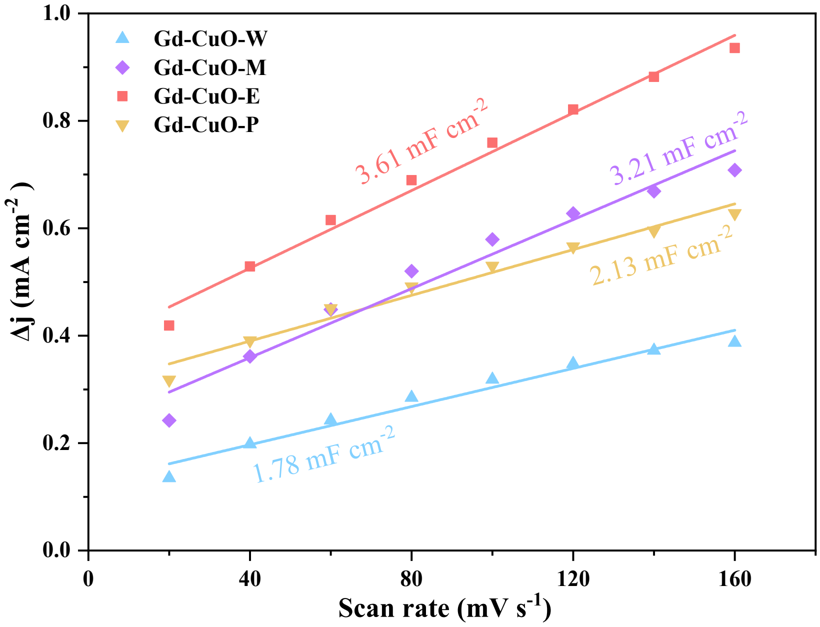


Figure S7. Capacitive currents at 0.51 V with different sweep rates of Gd-CuO-W, Gd-CuO-M, Gd-CuO-E, and Gd-CuO-P.

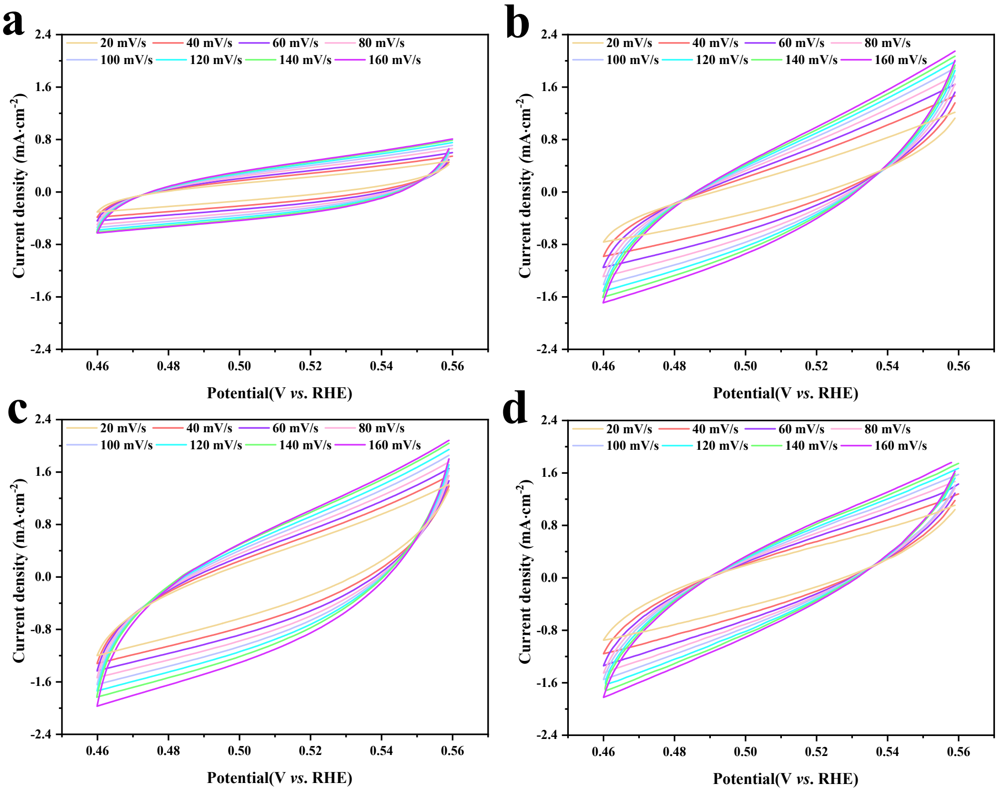


Figure S8. Cyclic voltammograms of Gd-CuO-W (a), Gd-CuO-M (b), Gd-CuO-E (c), and Gd-CuO-P (d) at different sweep rates.

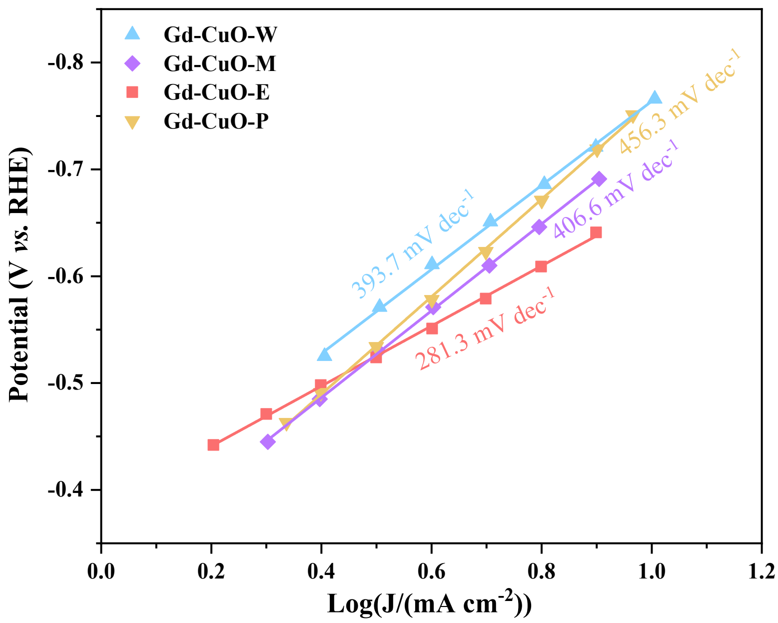


Figure S9. Tafel plots for Gd-CuO-W, Gd-CuO-M, Gd-CuO-E, and Gd-CuO-P.

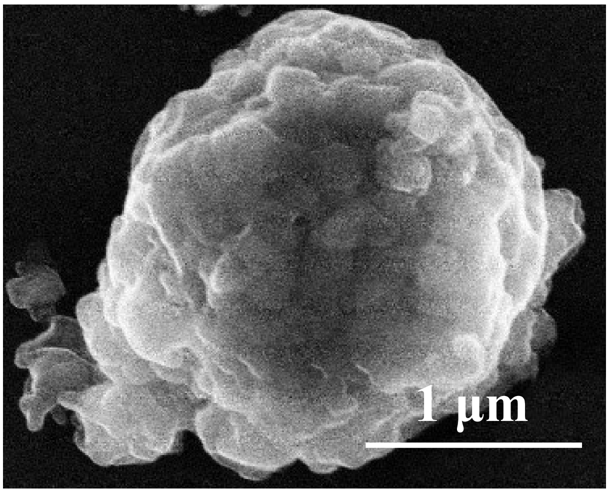


Figure S10. The SEM image of Gd-CuO-E after electrocatalytic CO_2RR.

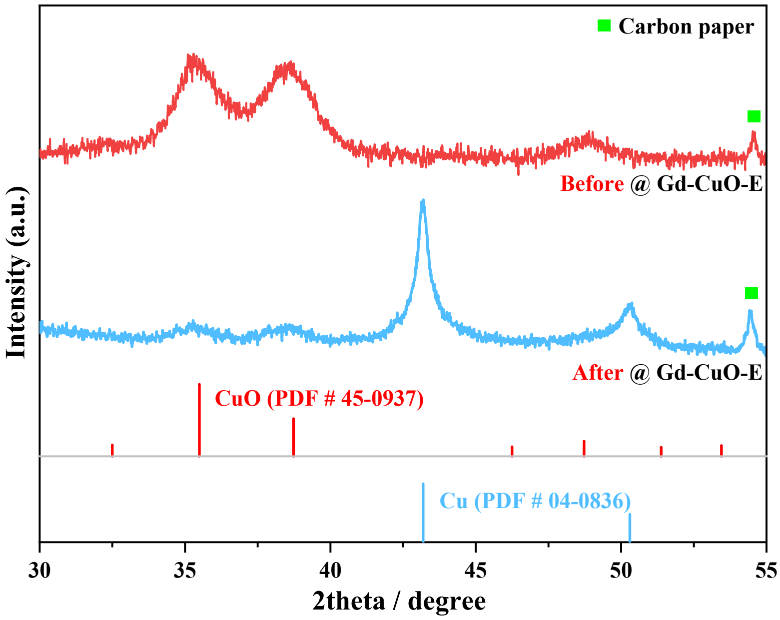


Figure S11. XRD patterns of Gd-CuO-E after electrocatalytic CO_2RR.

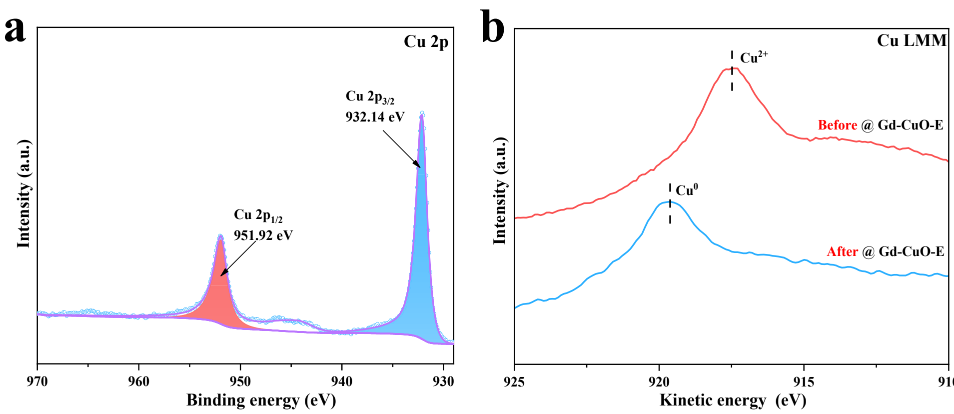
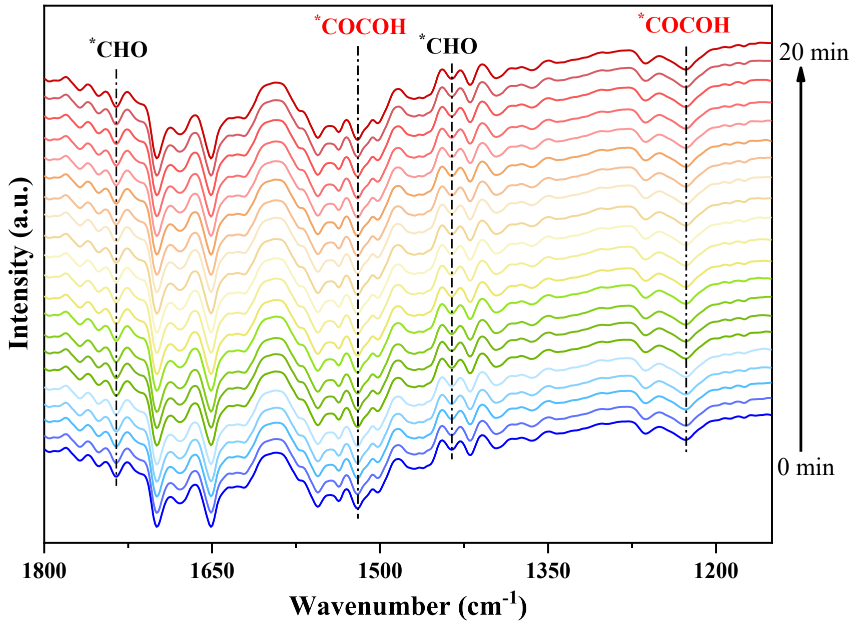


Figure S12. (a) Cu 2p XPS curve, and (b) Cu LMM Auger spectra of Gd-CuO-E after electrocatalytic CO_2RR.



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54 **Figure S13.** Time-dependent in situ ATR-FTIR spectra for CO_2RR on Gd-CuO-E.

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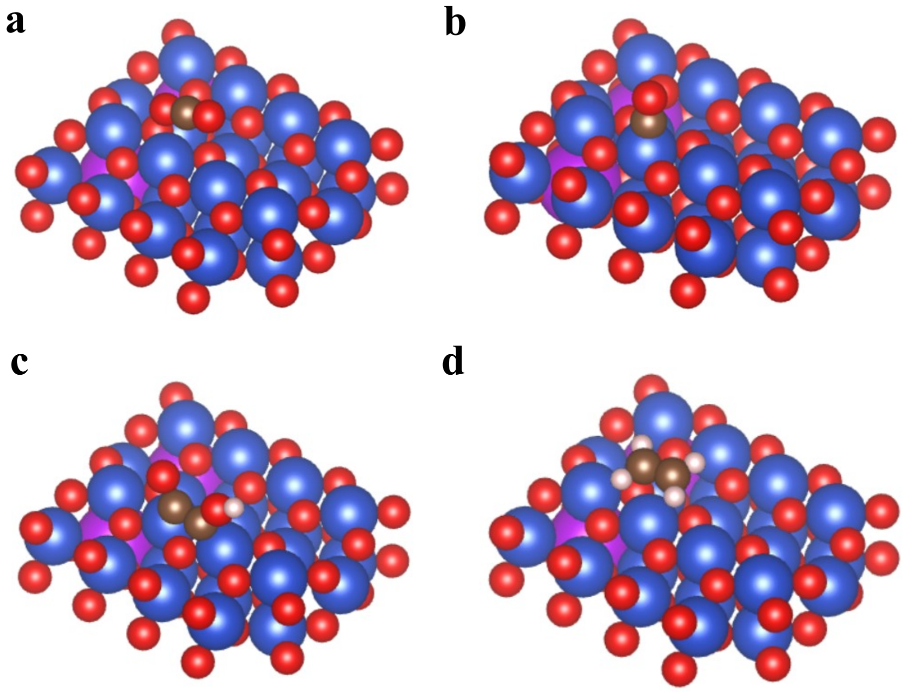

Figure S14. DFT calculation models of (a) *CO_2, (b) *CO, (c) *COCOH and (d) *C_2H_4 over Gd-CuO model. Cu: blue spheres; O: red spheres; Gd: purple spheres; C: brown spheres; H: white spheres.

Table S1. Elemental contents measured by SEM-mapping of Gd-CuO-E.

Element	Weight-percent (wt%)
Cu	67.58
O	26.18
Gd	6.24

Table S2. Catalyst particle size calculated by Scherrer's formula.

Catalyst	Catalyst particle size (Å)
Gd-CuO-W	109
Gd-CuO-M	101
Gd-CuO-E	55
Gd-CuO-P	44

Table S3. The comparison of the performance of electrocatalytic CO_2RR to ethylene on Gd-CuO-E with some representative Cu-based catalysts.

Samples	**E (V *vs.* RHE)**	**FE_{C2H4} (%)**	**Current density (mA cm^{-2})**	**cell type**	**ref**
CuO/CeO_2-SMSI	-1.16	50.5	18	H-cell	1
Cu-KOH/Ethanol-CV	-1.5	42.1	16.5	H-cell	2
CuO-PVDF	-1.12	32	3.8	H-cell	3
PTF(Ni)/Cu	-1.1	57.3	3.1	H-cell	4
Cu-$[CF_2]_n$-5-CP	-1.25	67.3	36.7	H-cell	5
PcCu-Cu-O	-1.2	50	7.3	H-cell	6
Pulsed copper foil	-1.0	50	15	H-cell	7
Cu_1Ni-BDP	-1.3	52.7	530	Flow-cell	8
Cu/Ni-NAC	-0.5	66	100	Flow-cell	9
TA-Cu	-1.2	63.6	497.2	Flow-cell	10
Gd-CuO-EtOH	-1.2	52.4	397.8	Flow-cell	**This work**
	-1.2	58.6	32.9	H-cell	

Table S4. The fitted results of EIS for four catalysts.

Catalyst	R_s	R_{ct}
Gd-CuO-W	4.93	12.98
Gd-CuO-M	5.14	11.10
Gd-CuO-E	3.34	10.95
Gd-CuO-P	5.26	15.38

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