Supporting Information

Rational Design of Organic Layer/3D Silver Foam Electrodes for Electrochemical CO_2 Reduction Reaction at Diluted Concentrations

*Kyeong-Nam Kang[†a,b], Dongyoon Shin[†a], Jihoon Kim[†a], Sang Heon Han[a], Jiseon Kim[a], Kyung Taek Woo[c], Seoungsoo Park[c], and Yun Jeong Hwang[*a,b]*

[a]Department of Chemistry, College of Natural Science, Seoul National University (SNU), Seoul 08826, Republic of Korea

[b]Center for Nanoparticle Research Institute for Basic Science (IBS), Seoul 08826, Republic of Korea

[c]KOGAS R&D Institute, Korea Gas Corporation, Ansan-si, Gyeonggi-do, 15328, Republic of Korea

† These authors contributed equally

e-mail address: yjhwang1@snu.ac.kr

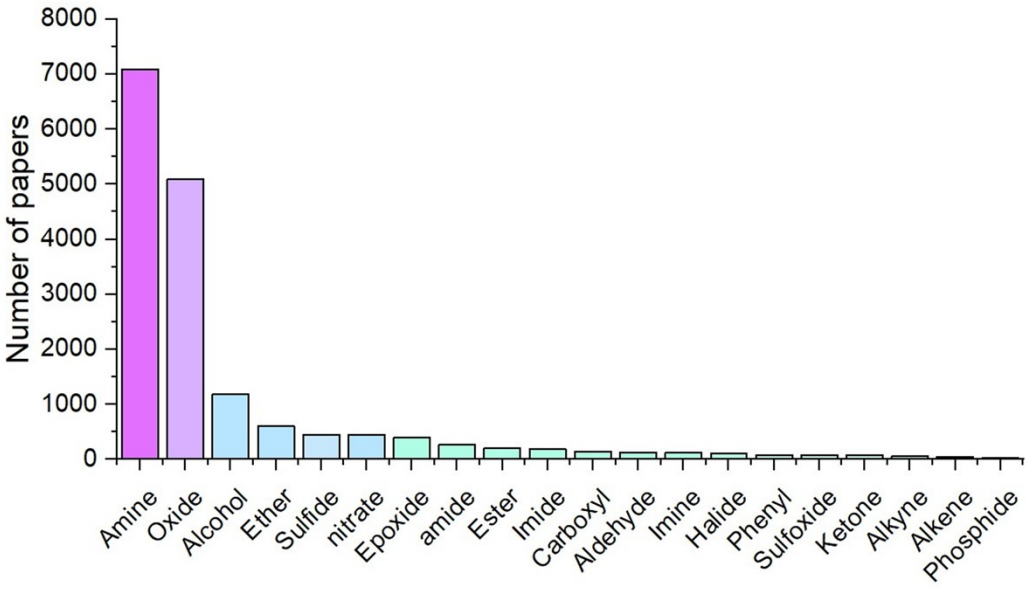


Fig. S1 Keyword search results of 20 different functional groups. Keywords were set as 'name of the functional group' and 'CO_2 capture', combined with a Boolean operator.

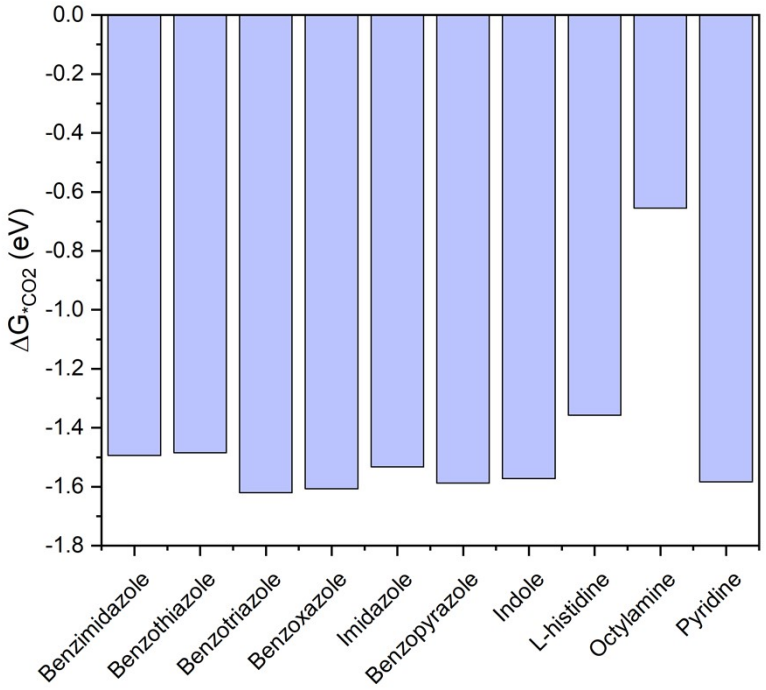


Fig. S2. CO_2 adsorption energy values of various molecules.

Table S1. List of molecules and their abbreviations.

Name	Abbreviation
Benzoxazole	BO
Benzothiazole	BT
L-histidine	His
Benzimidazole	BI
Indole	In
Benzopyrazole	BP
Benzotriazole	BTr
Imidazole	Im
Pyridine	Py
Octylamine	OA

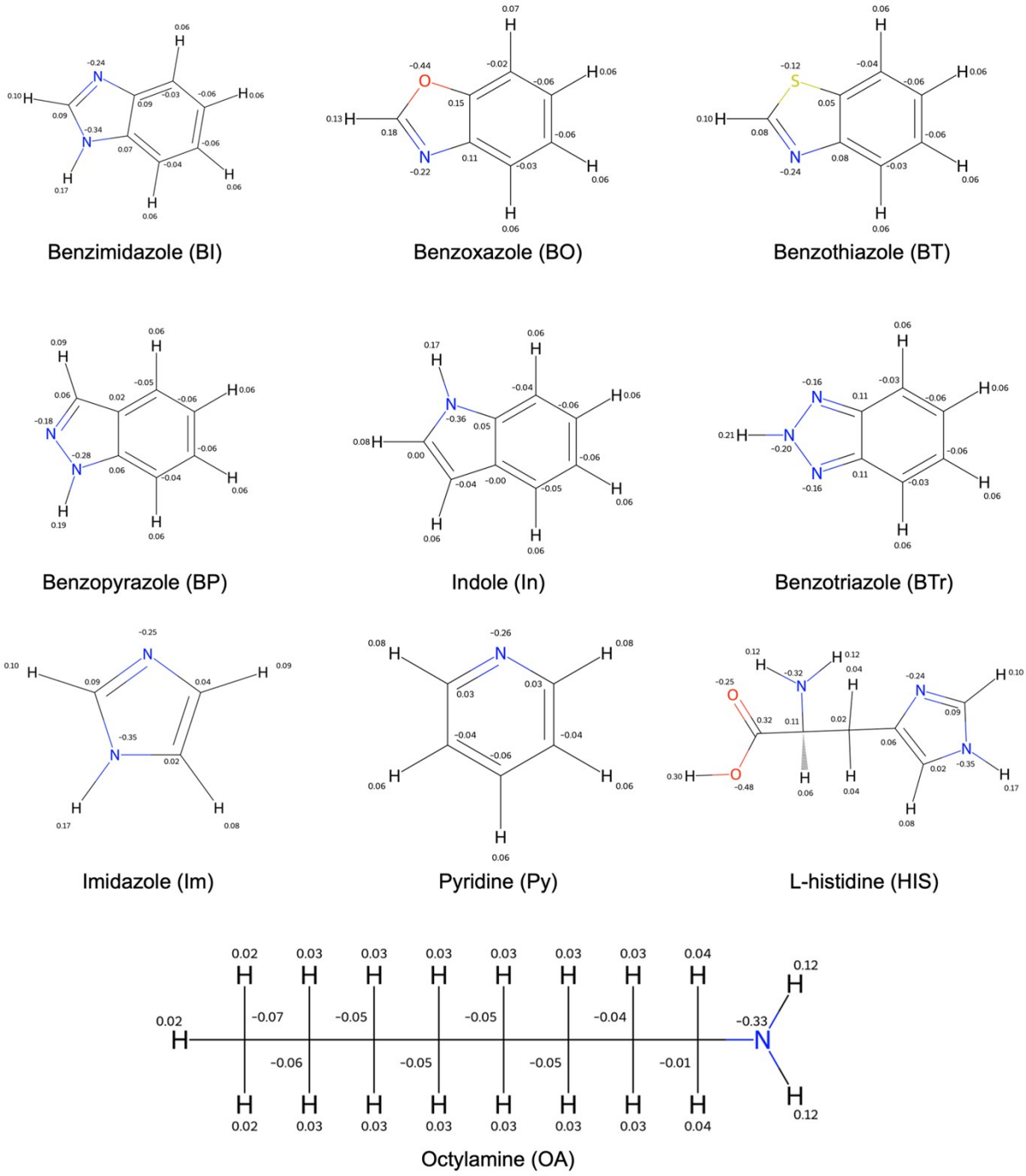


Fig. S3 Partial charges of candidate molecules.

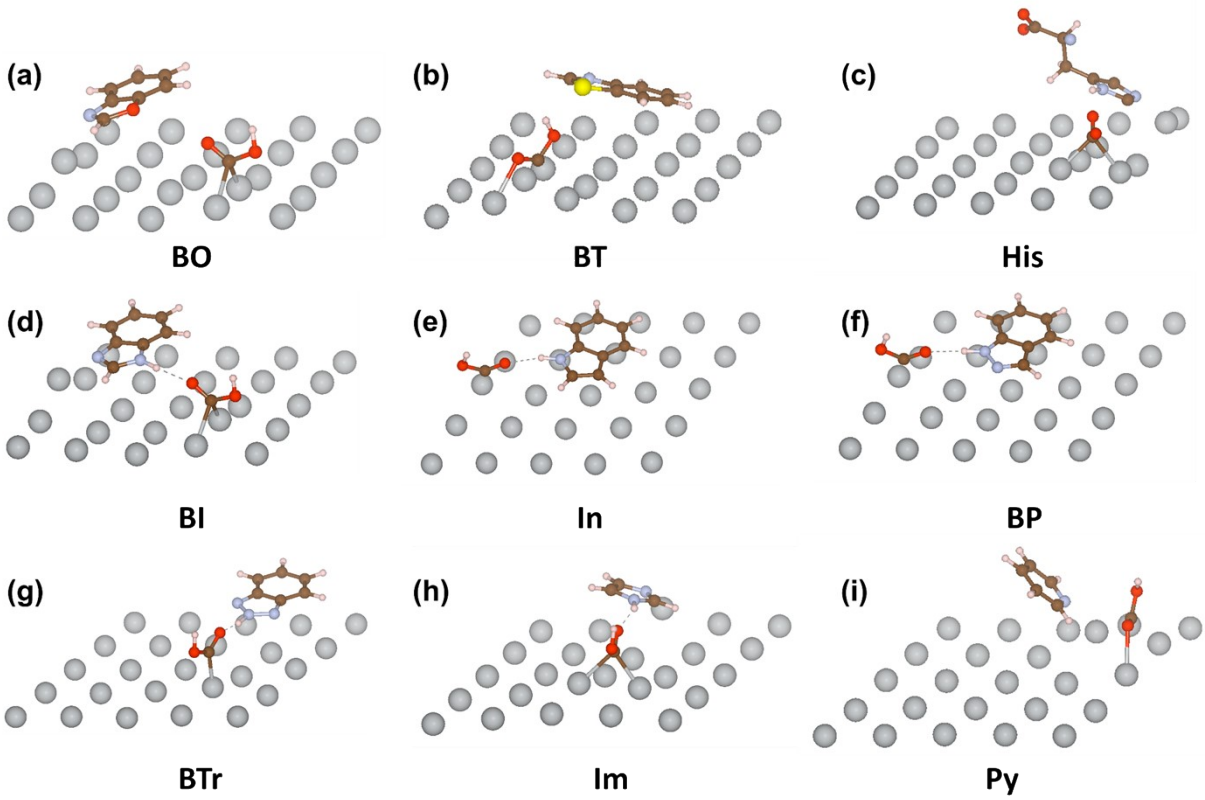


Fig. S4 Relaxed structures of *COOH-adsorbed surface with 9 candidate molecules. Atoms are represented in different colors (brown: C, White: H, sky blue: N, red: O, yellow: S and gray: Ag). (a) Benzoxazole (BO), (b) Benzothiazole (BT), (c) *L*-Histidine (His), (d) Benzimidazole (BI), (e) Indole (In), (f) Benzopyrazole (BP), (g) Benzotriazole (BTr), (h) Imidazole (Im), (i) Pyridine (Py).

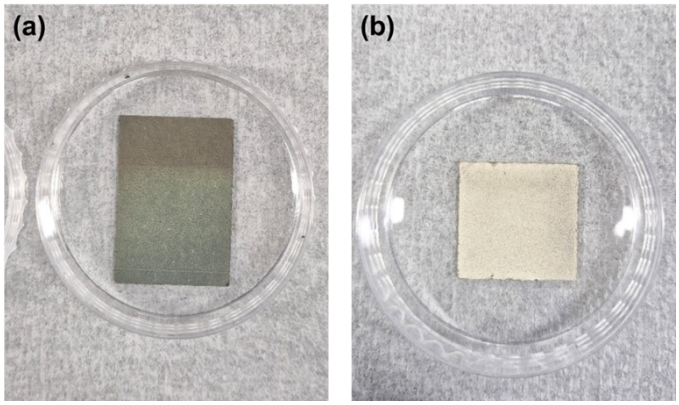


Fig. S5 Digital images of (a) sputtered Ag onto the benzimidazole layer-coated GDE (BI-Ag) and (b) Ag foam electrodeposited onto BI-Ag (denoted as BI-*sf*).

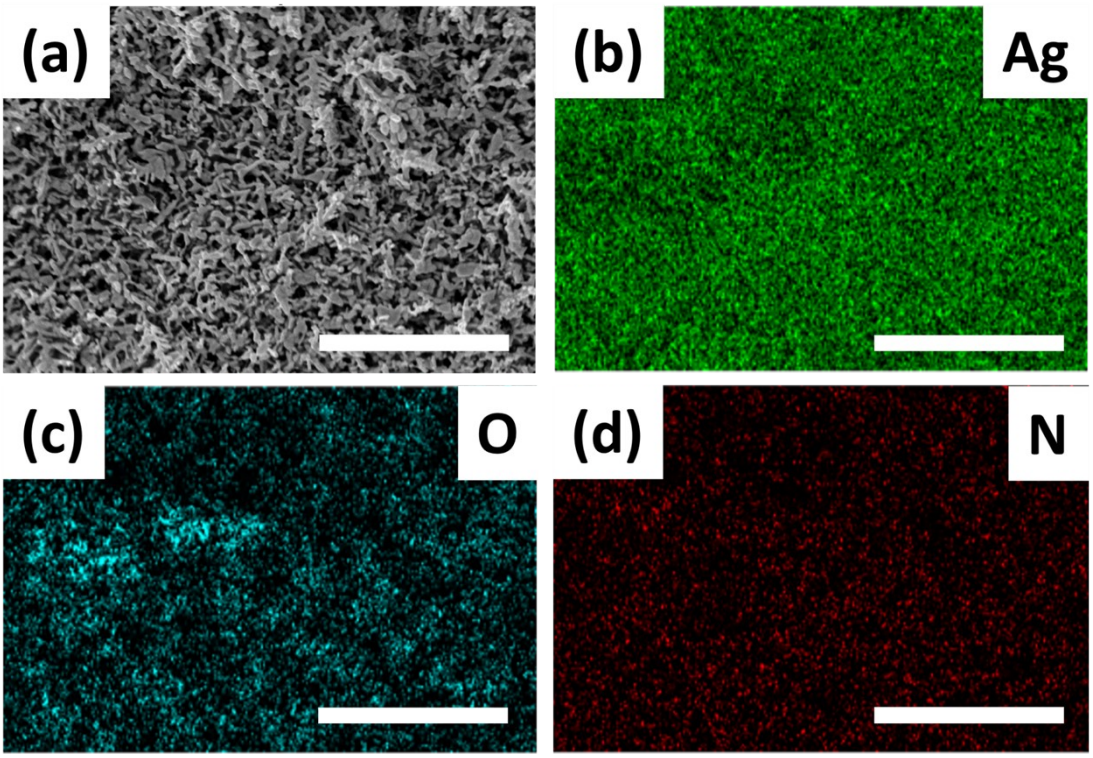


Fig. S6 Total EDS elemental mapping images of (a) the as-prepared BI-*sf* and the detail peaks for (b) Ag, (c) O, and (d) N. scale bar: 10 μm

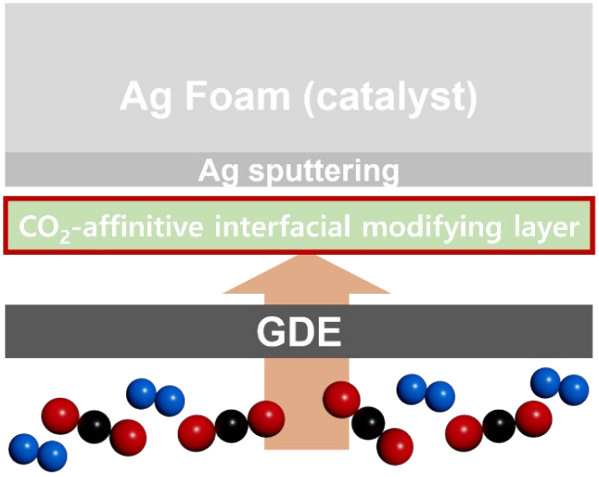


Fig. S7 Schematic diagram of the concept of the BI-*sf.* CO_2-affinitive interfacial modifier: benzimidazole layer (BI).

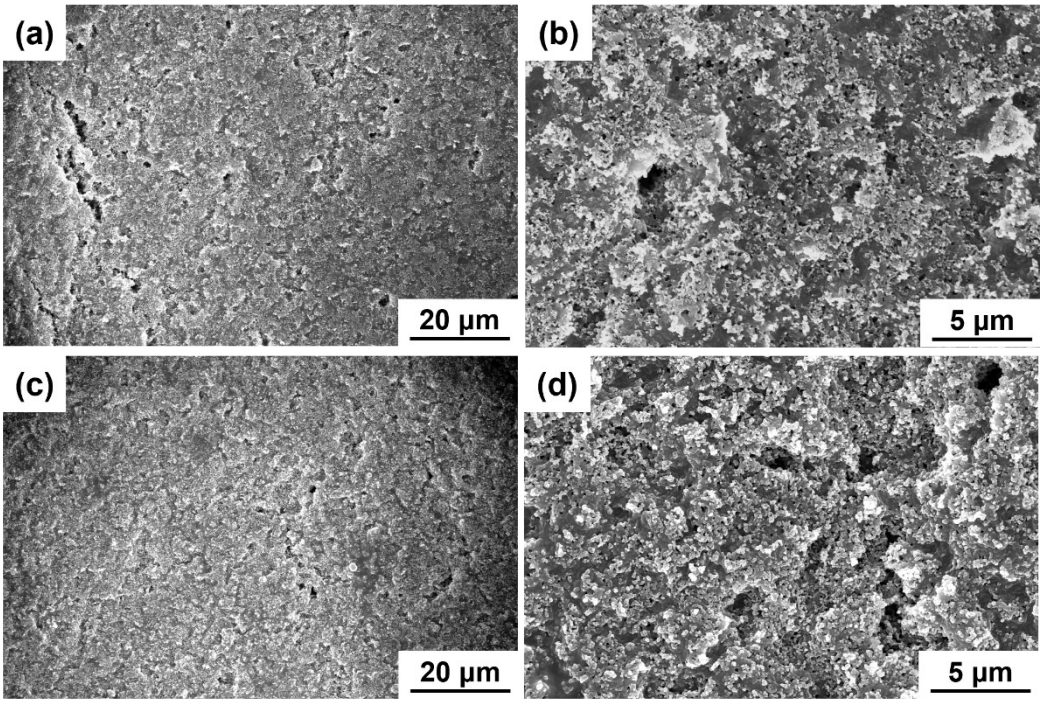


Fig. S8 Top-view SEM images of the bare GDE (a, b) and BI-coated electrode (c, d).

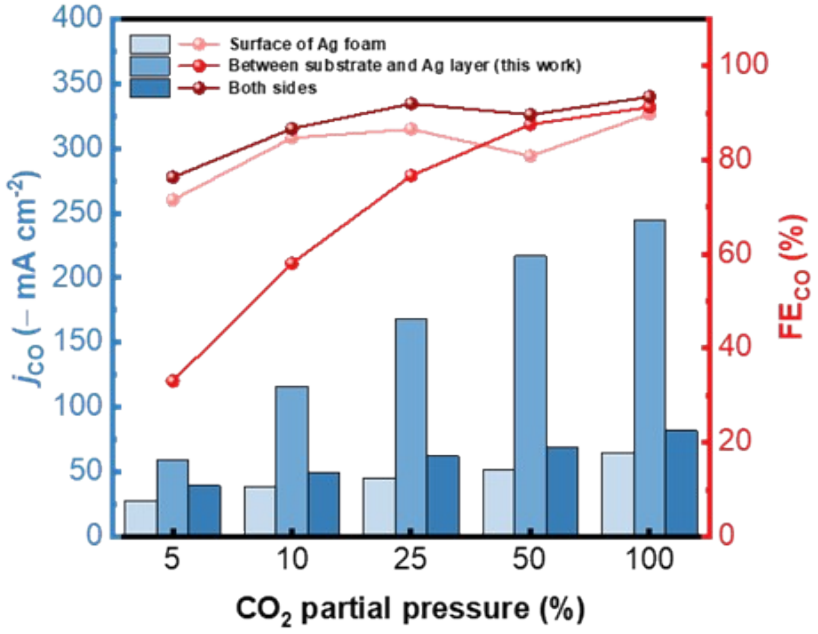


Fig. S9. Current densities and Faradaic efficiencies (FE) of three electrodes with different BI coating positions as a function of CO_2 concentrations.

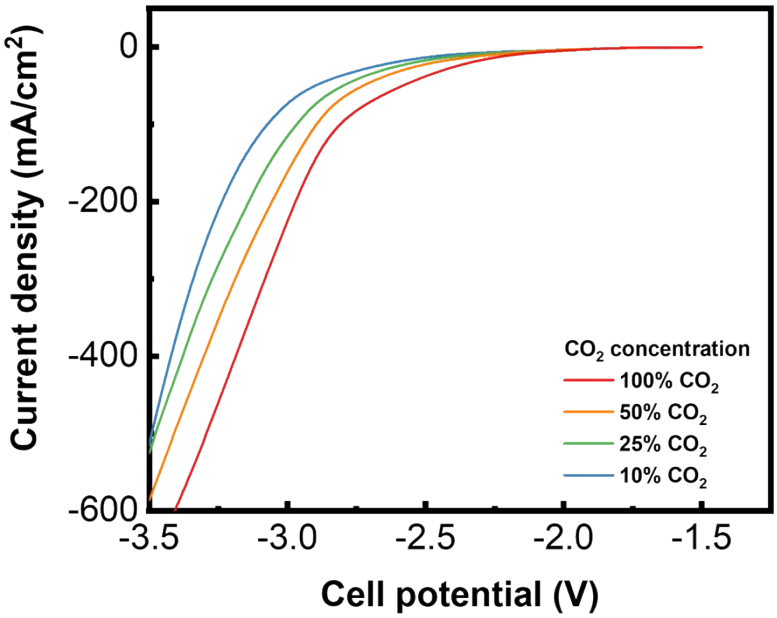


Fig. S10 LSV curves measured with BI-*sf* electrode at various CO_2 concentrations

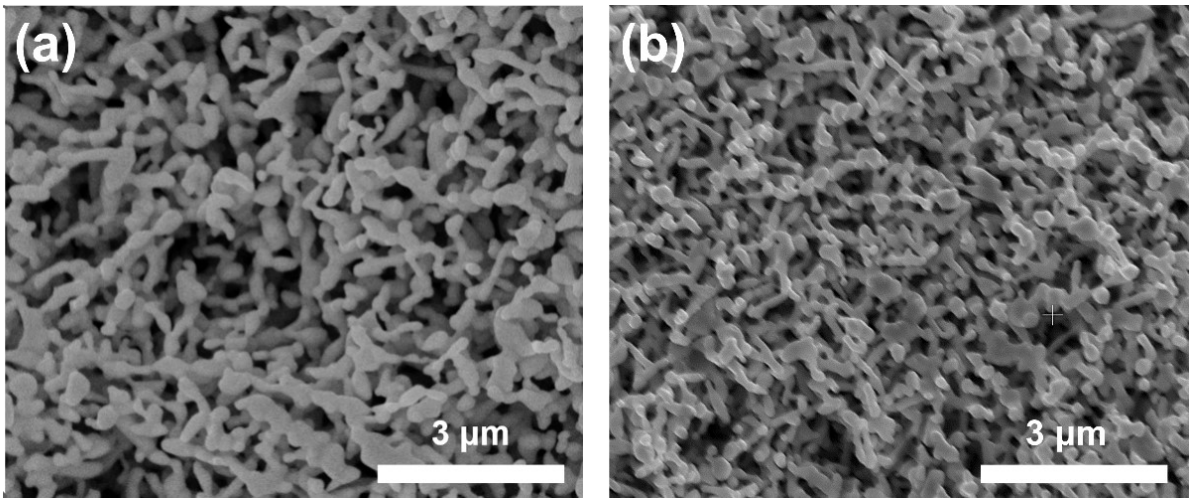


Fig. S11 SEM images of the Bi-sf electrode (a) before and (b) after long-term stability test.

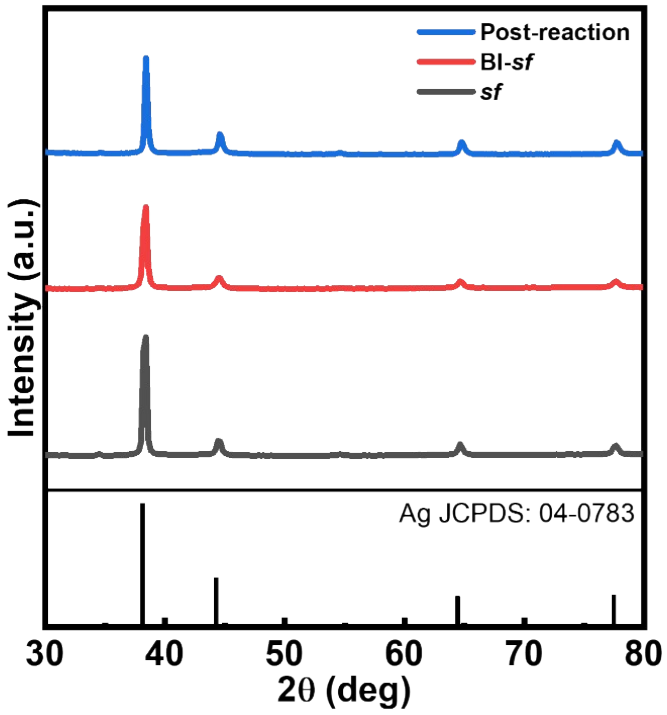
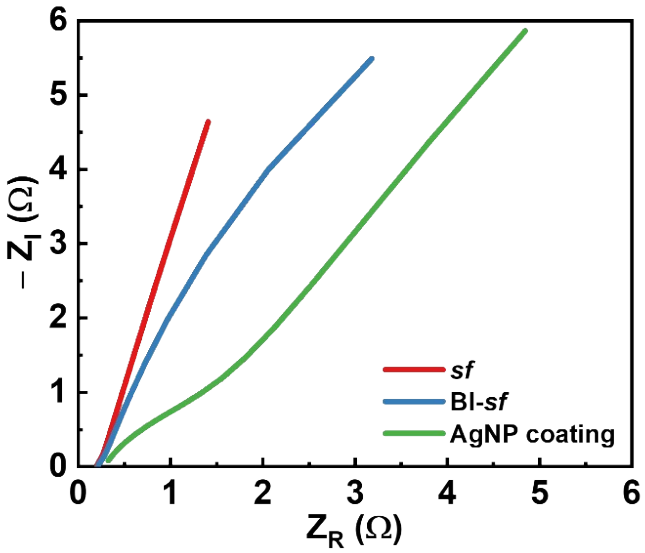


Fig. S12 XRD patterns of sf, BI-sf, and BI-sf after long-term stability test.



	sf	BI-sf	AgNP coating
R_s (Ω)	0.20	0.21	0.28
R_{ct} (Ω)	0.034	0.065	0.930

Fig. S13 Comparison of Nyquist plots of AgNP-coated electrode, sf, and BI-sf

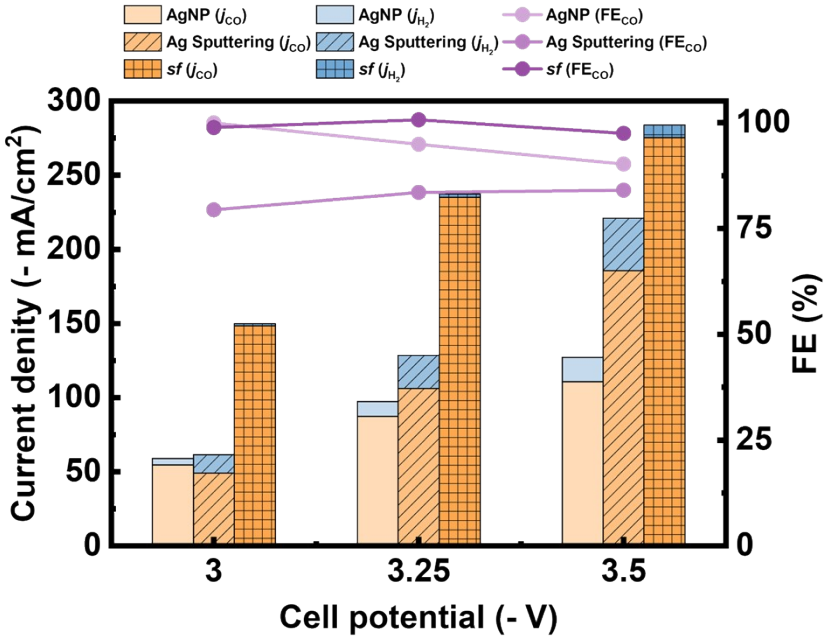


Fig. S14 Current densities and Faradaic efficiencies (FE) of AgNP, sputtered Ag, and Ag foam deposited on GDE carbon paper electrode as a function of the controlled cell potential measured under 100% CO_2 conditions.

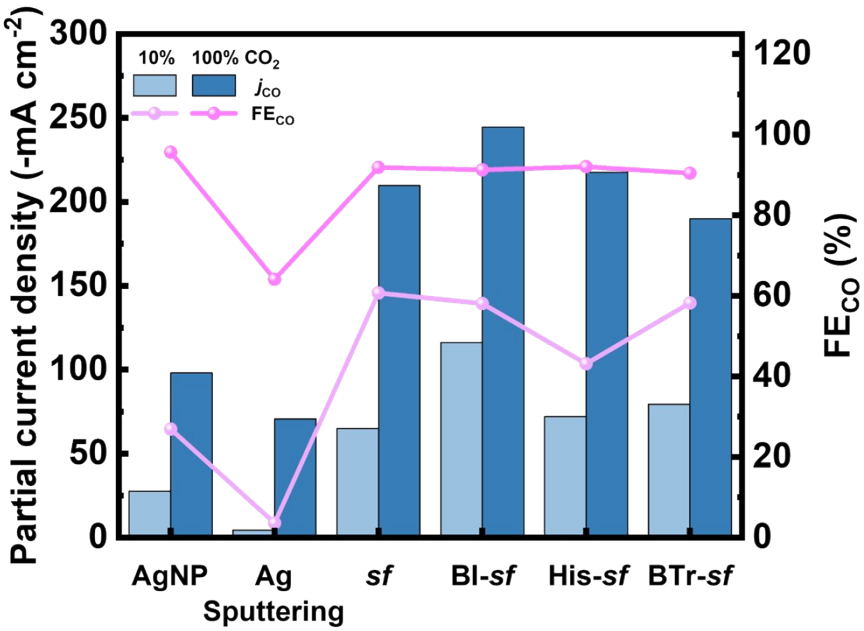


Fig. S15 CO_2RR performances of the electrodes at 10 % and 100 % CO_2 conditions. All measurements were taken in a MEA setup at -3.25 V cell potential.

Table. S2 Silver-based catalysts under dilute CO_2 conditions by zero-gap membrane electrode assembly (MEA); Comparison table of Faradaic efficiency (FE_{CO}) and efficiency retention after long-term stability

Electrode	FE_{CO}	Long-term stability (FE_{CO})	
Ag	• About 70.0 % (100 % CO_2) • 5.4 % (20 % CO_2)	28.5 % retention (9 hr)	[1]
Ag/Nafion	• About 90.0 % (100 % CO_2) • 45.1 % (20 % CO_2)	82.5 % retention (62 hr)	[1]
Ag/PTFE	• 85.0 % (100 % CO_2) • 39.0 % (20 % CO_2)	78.0 % retention (62 hr)	[1]
Ag-C	• 97.5 % (100 % CO_2) • 23.0 % (10 % CO_2)	63.5 % retention (100 hr)	[2]
Ag/C	• 97.5 % (100 % CO_2) • 29.0 % (10 % CO_2)	Almost 100 % retention (600 hr)	[2]
Ag@C	• 97.5 % (100 % CO_2) • 19.0 % (10 % CO_2)	87.6 % retention (100 hr)	[2]
BI-*sf* (This work)	• 91.9 % (100 % CO_2) • 87.1 % (25 % CO_2) • 49.7 % (10 % CO_2)	Almost 100 % retention (45 hr)	

Table S3 Current densities and Faradaic efficiencies (FE) of Bi-sf at a cell potential of -3.25 V under atmospheric CO_2 levels.

Concentration (ppm)	j_{CO} (– mA cm^{-2})	FE_{CO} (%)	FE_{Tot} (%)
5000	2.766	1.426	99.74
2500	0.893	0.852	99.79
1000	0.086	0.065	99.87
650	0.094	0.065	100.01

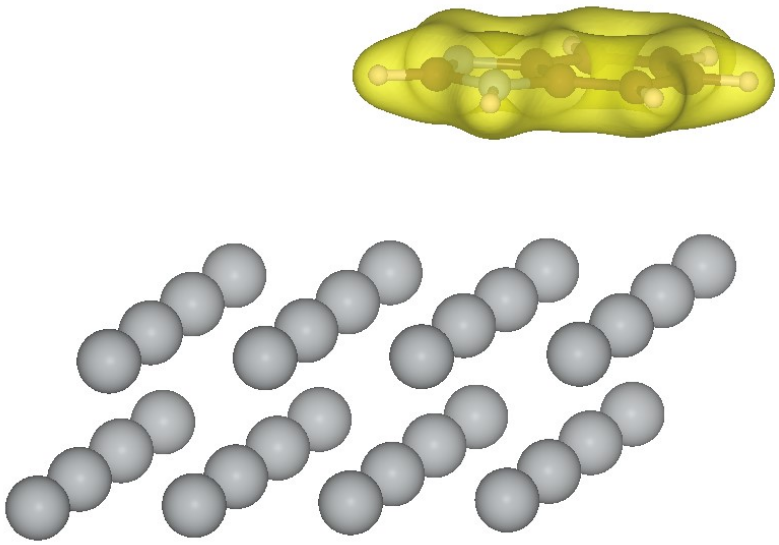


Fig. S16. Visualization of charge delocalization throughout the BI molecule. Isosurface was drawn with a threshold of 0.05 e^{-} $Å^{-3}$.

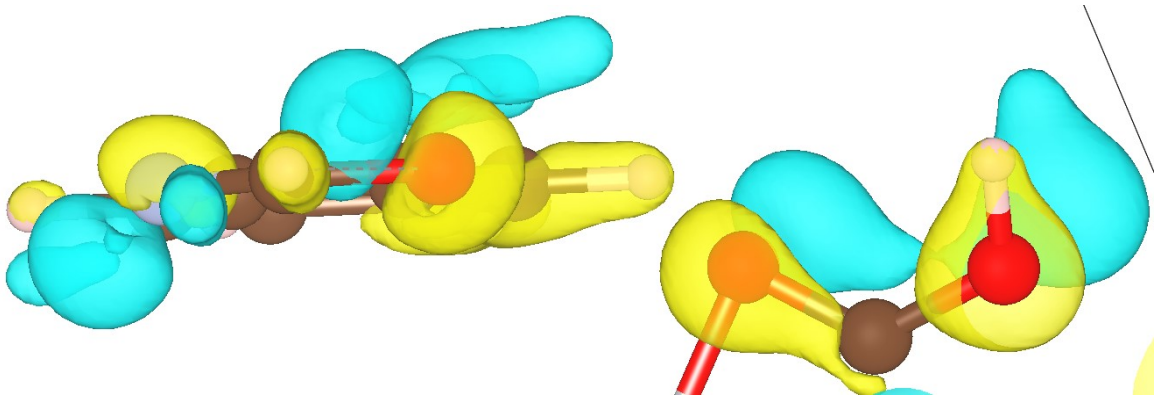


Fig. S17 Charge density difference plot displaying the interaction between benzimidazole – COOH on top of the Ag surface.

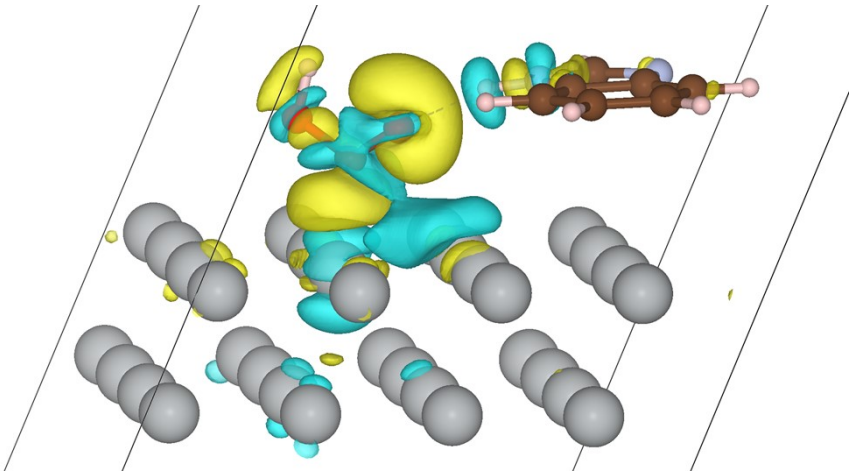


Fig. S18 Charge density difference plot displaying the interaction between benzimidazole – COOH on top of the Ag surface.

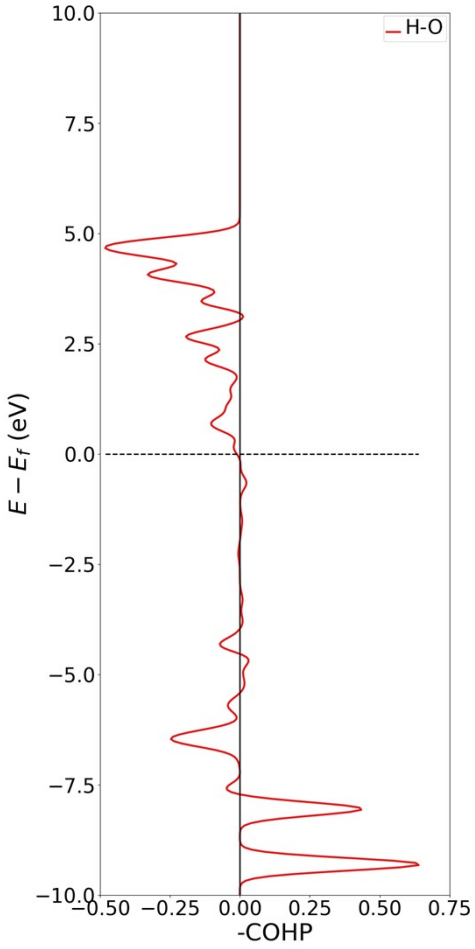


Fig. S19 Crystal orbital Hamilton population (COHP) with respect to E – E_f for the O-H hydrogen bond. The negative integrated value of COHP (-ICOHP) for benzimidazole – COOH is -0.65 eV.

References

[1] Q. Chang, G. Zhang, J. Chen, X. Du, C. Wang, Y. Cai, Y. Du, P. Zhang, T. Wang, J. Gong, *J. Energy Chem.* 108 (**2025**) 373-380

[2] M. Zhang, G. Zhang, H. Gao, X. Du, C. Wang, T. Wang, P. Zhang, J. Gong, *ChemSusChem* **2024**, 17, e202400093