Supplementary Information for

Synthesis of Heterometallic Metal-Organic Frameworks and their Performance as Electrocatalyst for CO_2 Reduction

Maite Perfecto-Irigaray,[a] Jonathan Albo,[b,*] Garikoitz Beobide,[a,*] Oscar Castillo,[a] Angel Irabien[b] and Sonia Pérez-Yáñez[a,c]

[a] *Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco/Euskal Herriko Unibertsitatea, UPV/EHU, Apartado 644, E-48080 Bilbao, Spain.*
[b] *Department of Chemical & Biomolecular Engineering, University of Cantabria (UC), Avda. Los Castros, 39005, Santander (Spain)*
[c] *Departamento de Química Inorgánica, Facultad de Farmacia, Universidad del País Vasco/Euskal Herriko Unibertsitatea, UPV/EHU, E-01006 Vitoria-Gasteiz, Spain.*

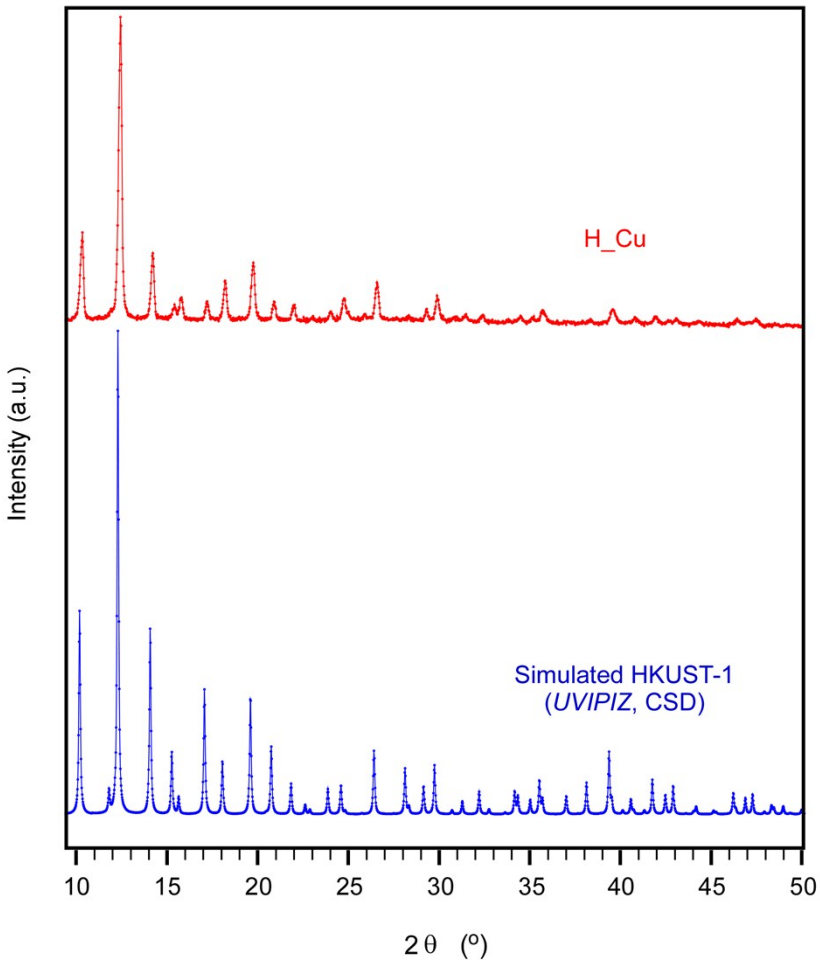
S1. SOLVENT-FREE SYNTHESIS OF PRISTINE AND DOPED SAMPLES

The synthesis procedure was performed as described in the manuscript. Table S1 gathers the reagent amounts, doping target ratio, achieved doping ratio and reaction yield for each sample.

Table S1. Molar content (%) of the metal dopant (M_D) in the synthesis mixture and in the products, and synthesis yield (%).

M	Reagents	Synthesis M_D : Cu ratio	Product M_D : Cu ratio	Sample code	Yield (%)
--	$Cu(OAc)_2$: 0.6120 mmol (0.1234 g) H_3BTC: 0.4063 mmol (0.0899 g)	0 : 100	0 : 100	H_Cu	90
Zn	$Cu(OAc)_2$: 0.5730 mmol (0.1156 g) H_3BTC: 0.4011 mmol (0.08873 g) $Zn(OAc)_2 \cdot 2H_2O$: 0.0382 mmol (0.0084 g)	5 : 95	5 : 95	H_Zn5	70
	$Cu(OAc)_2$: 0.5474 mmol (0.1093 g) H_3BTC: 0.4007 mmol (0.08864 g) $Zn(OAc)_2 \cdot 2H_2O$: 0.0619 mmol (0.0137 g)	10 : 90	8 : 92	H_Zn8	88
	$Cu(OAc)_2$: 0.4952 mmol (0.0989 g) H_3BTC: 0.4088 mmol (0.0904 g) $Zn(OAc)_2 \cdot 2H_2O$: 0.1202 mmol (0.0266 g)	20 : 80	19 : 81	H_Zn19	75
Ru	$Cu(OAc)_2$: 0.5825 mmol (0.1163 g) H_3BTC: 0.4015 mmol (0.0888 g) $RuCl_3 \cdot xH_2O$: 0.0314 mmol (0.0065 g)	5 : 95	3 : 97	H_Ru3	86
	$Cu(OAc)_2$: 0.5470 mmol (0.1092 g) H_3BTC: 0.4007 mmol (0.0887 g) $RuCl_3 \cdot xH_2O$: 0.0624 mmol (0.0130 g)	10 : 90	7 : 93	H_Ru7	89
	$Cu(OAc)_2$: 0.4888 mmol (0.0976 g) H_3BTC: 0.4034 mmol (0.0892 g) $RuCl_3 \cdot xH_2O$: 0.1267 mmol (0.0263 g)	20 : 80	10 : 90	H_Ru10	83
Pd	$Cu(OAc)_2$: 0.5911 mmol (0.1180 g) H_3BTC: 0.4075 mmol (0.0901 g) $Pd(OAc)_2$: 0.0317 mmol (0.0072 g)	5 : 95	3: 97	H_Pd3	85
	$Cu(OAc)_2$: 0.5492 mmol (0.1097 g) H_3BTC: 0.4002 mmol (0.0885 g) $Pd(OAc)_2$: 0.0616 mmol (0.0141 g)	10 : 90	5 : 95	H_Pd5	79
	$Cu(OAc)_2$: 0.4944 mmol (0.0987 g) H_3BTC: 0.4027 mmol (0.0891 g) $Pd(OAc)_2$: 0.1239 mmol (0.0284 g)	20 : 80	11 : 89	H_Pd11	77

S2. X-RAY POWDER DIFFRACTION ANALYSIS



UVIPIZ	
Crystal system	Cubic
Space group	F m$\bar{3}$m
a (A)	26.361
V (A3)	18 317
T (K)	295

Figure S1. Experimental and simulated X-ray diffraction patterns for undoped H_Cu sample.

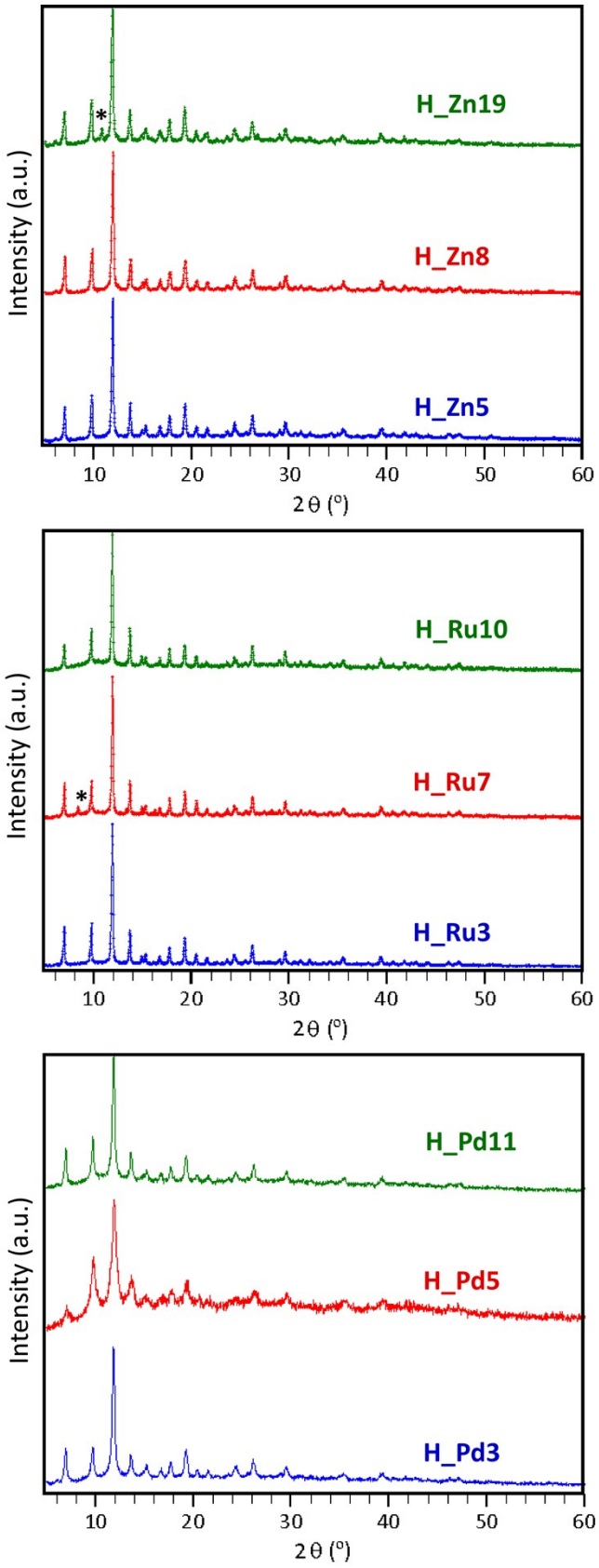
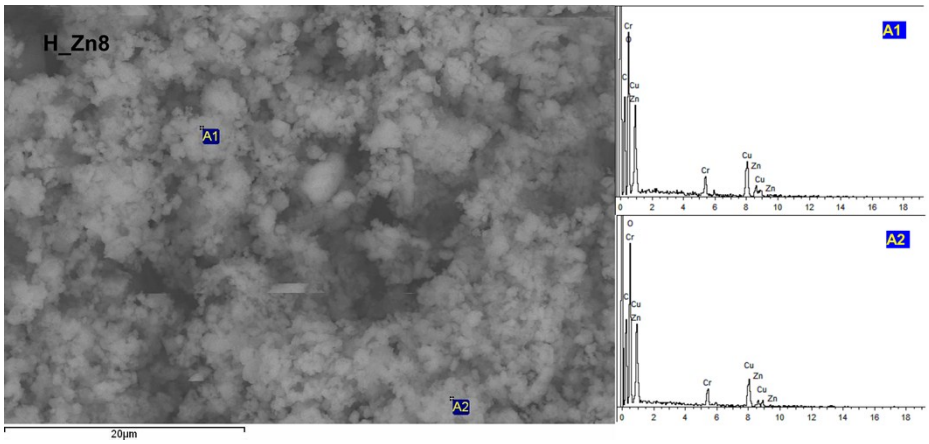
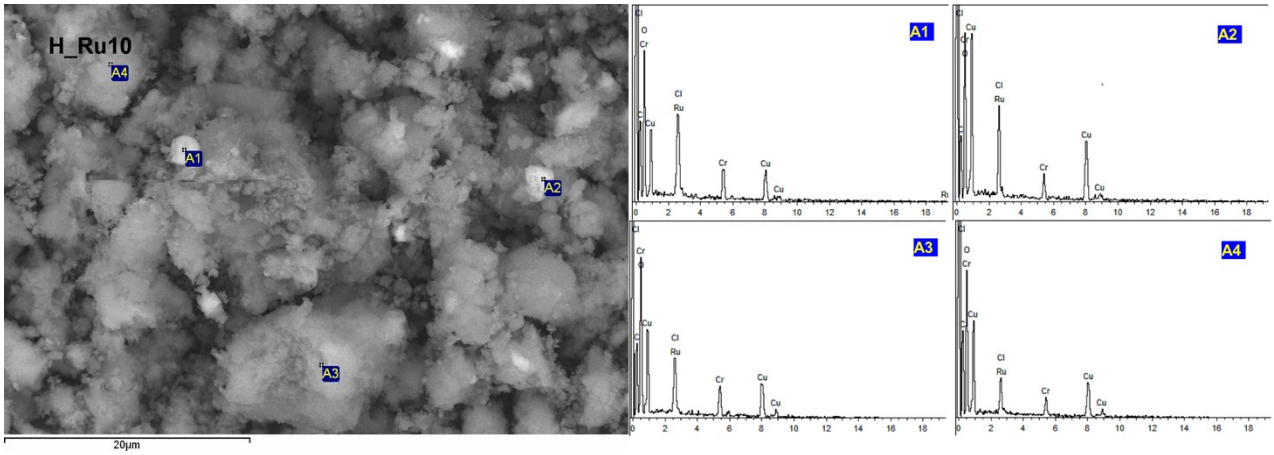


Figure S2. X-ray diffraction patterns for H_M_DX samples. Asterisk marks stand for unidentified M/BTC impurities.

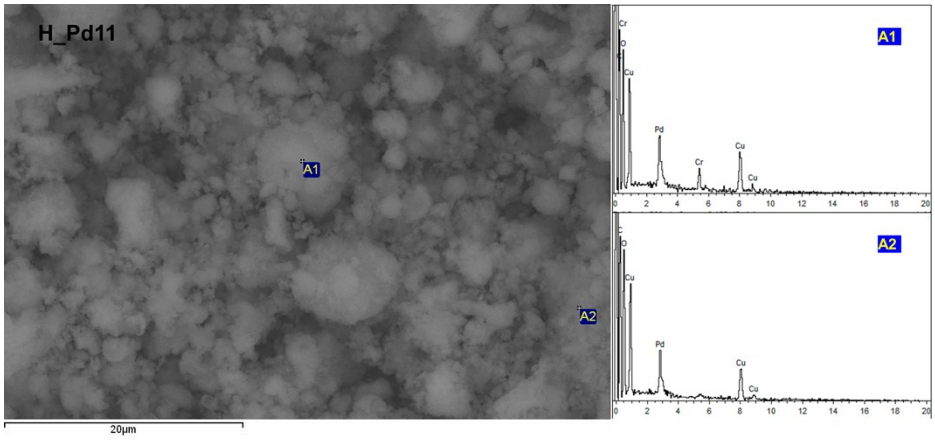
S3. SCANNING ELECTRON MICROSCOPY DATA



(a)



(b)



(c)

Figure S3. SEM and correspond EDX analysis obtained for H_M_D samples: (a) 8 % of Zn, (b) 10 % of Ru, (c) 11 % of Pd; each of one homogeneously distributed in the sample.

S4. QUANTITATIVE DATA ON CO_2 ELECTROREDUCTION

Table S2. r and FE in the electrocatalytic conversion of CO_2 at MOF-GDEs.

MOF-GDEs	E (V)	r (10^{-5} mol·m^{-2}·s^{-1})			FE (%)		
		CH_3OH	C_2H_5OH	TOTAL	CH_3OH	C_2H_5OH	TOTAL
H_Cu	1.77	0.87	1.79	2.66	2.51	10.37	12.87
H_Zn5	1.87	-	2.16	2.16	-	12.51	12.51
H_Zn8	1.79	-	2.22	2.22	-	12.85	12.85
H_Zn19	1.73	-	1.86	1.86	-	10.75	10.75
H_Ru3	1.84	0.37	2.14	2.51	1.07	10.22	11.29
H_Ru7	1.72	0.13	1.65	1.78	0.36	9.58	9.94
H_Ru10	1.73	-	1.41	1.41	-	8.18	8.18
H_Pd3	1.88	0.86	0.71	1.57	0.44	4.10	4.54
H_Pd5	1.89	-	0.77	0.77	-	4.46	4.46
H_Pd11	1.93	-	0.65	0.65	-	3.73	3.73

S5. X-RAY POWDER DIFFRACTION ANALYSIS ON MOF-GDES

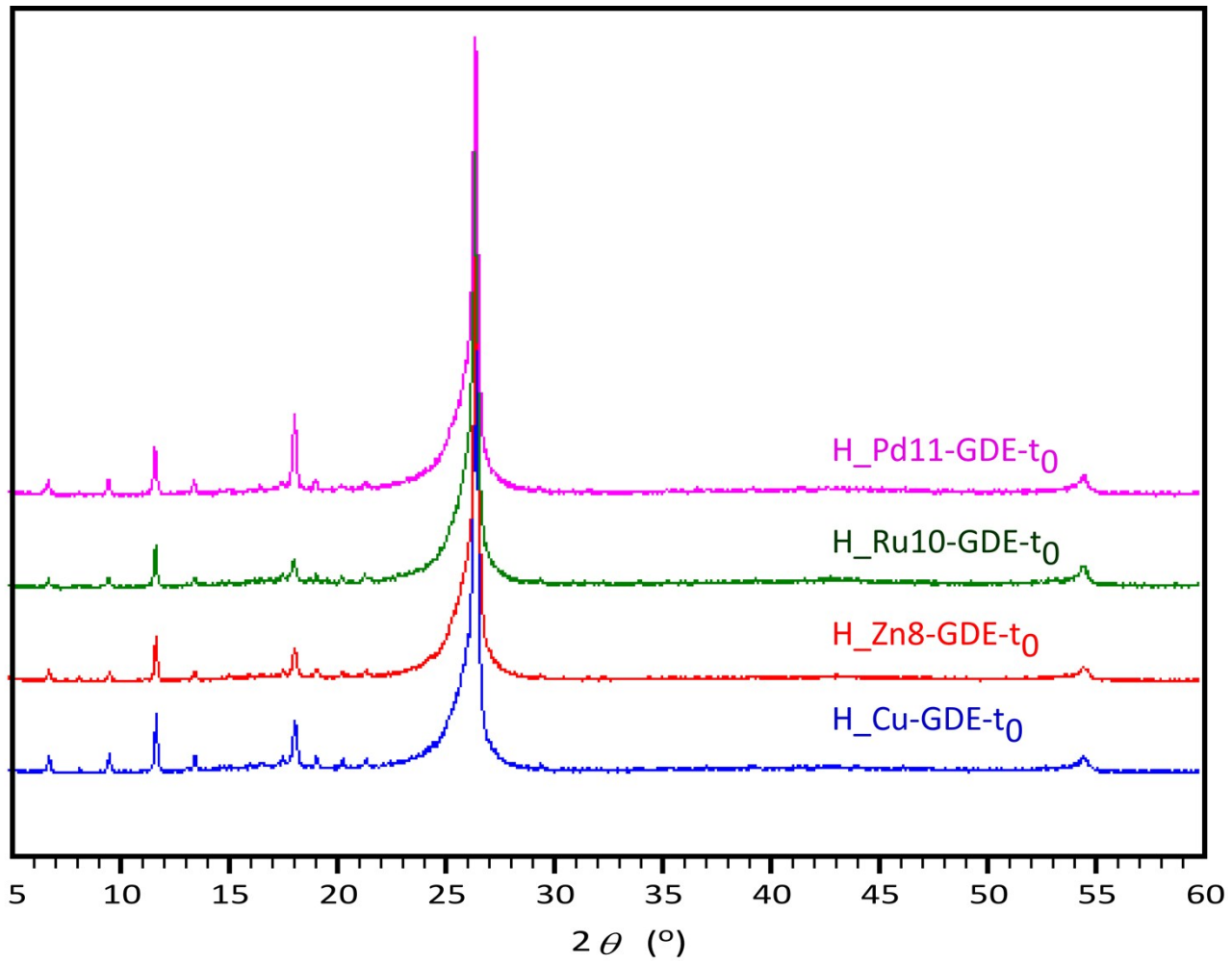


Figure S4. X-ray diffraction patterns for H_M_DX-GDE samples before electrochemical evaluation, where correspond peaks to HKUST-1 type structure are identified. Peaks on 26 º and 54,5 º (2θ) correspond to graphite from the electrode preparation.