

Commuting CO₂ Electro-Reduction Active Sites on a Nickel-Based Hybrid Formed on a "Guilty" Covalent Triazine Framework

Giulia Tuci,^{*[a]} Miriam Moro,^[b] Andrea Rossin,^[a] Claudio Evangelisti,^[c] Lorenzo Poggini,^[a, d]

Marco Etzi,^[e] Enrico Verlato,^[f] Francesco Paolucci,^[b, f, g] Yuefeng Liu,^[h] Giovanni Valenti^{*[b, g]}

Giuliano Giambastiani ^{*[d, a]}

^[a] *Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR and Consorzio INSTM, Via Madonna del Piano, 10 – 50019, Sesto F.no, Florence, Italy.*

^[b] *Department of Chemistry “Giacomo Ciamician”, University of Bologna, Via Piero Gobetti 85, 40129 Bologna, Italy.*

^[c] *Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR, Via G. Moruzzi, 1 – 56124 Pisa, Italy.*

^[d] *University of Florence, Department of Chemistry “U. Schiff” - DICUS – and INSTM Research Unit, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI), Italy.*

^[e] *Center for Sustainable Future Technologies, Fondazione Istituto Italiano di Tecnologia, Via Livorno 60, Torino, 10144, Italy*

^[f] *Institute of Condensed Matter Chemistry and Technologies for Energy, ICMATE-CNR, 35127 Padova, Italy*

^[g] *Center for Chemical Catalysis – C3, Alma Mater Studiorum – Università di Bologna, Via Gobetti 85, 40129 Bologna, Italy*

^[h] *Dalian National Laboratory for Clean Energy (DNL), Dalian Institute of Chemical Physics, Chinese Academy of Science, 457 Zhongshan Road, 116023 Dalian, China*

Supporting Information

Table S1. Textural properties of CTF^{ph} and Ni/CTF^{ph} at comparison.

Sample	Ni ^a (wt.%)	Materials textural properties ^b		
		surface area (m ² /g)	Micropore volume (cm ³ /g)	total pore volume (cm ³ /g)
CTF ^{ph}	-	2046 ^c	0.51	1.55 ^c
Ni/CTF ^{ph} (1)	9.2	1897	0.46	1.32

^a determined by ICP-OES; ^b derived from N₂ physisorption isotherms recorded at the liquid N₂ temperature along with the respective pore-size distributions (BJH method) from isotherms desorption branches. ^c data recovered from ref. 1 and reported here for the sake of comparison.

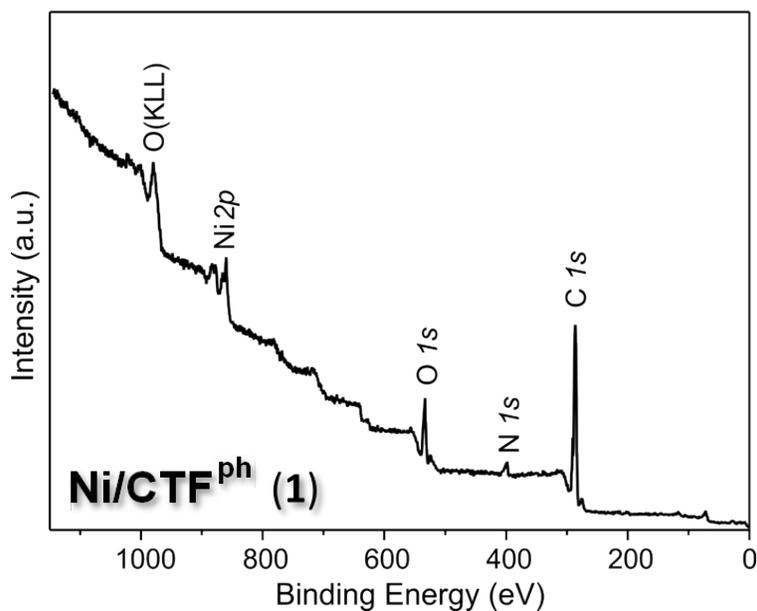


Fig. S1. XPS survey spectrum of Ni/CTF^{ph} (1).

Supporting Information

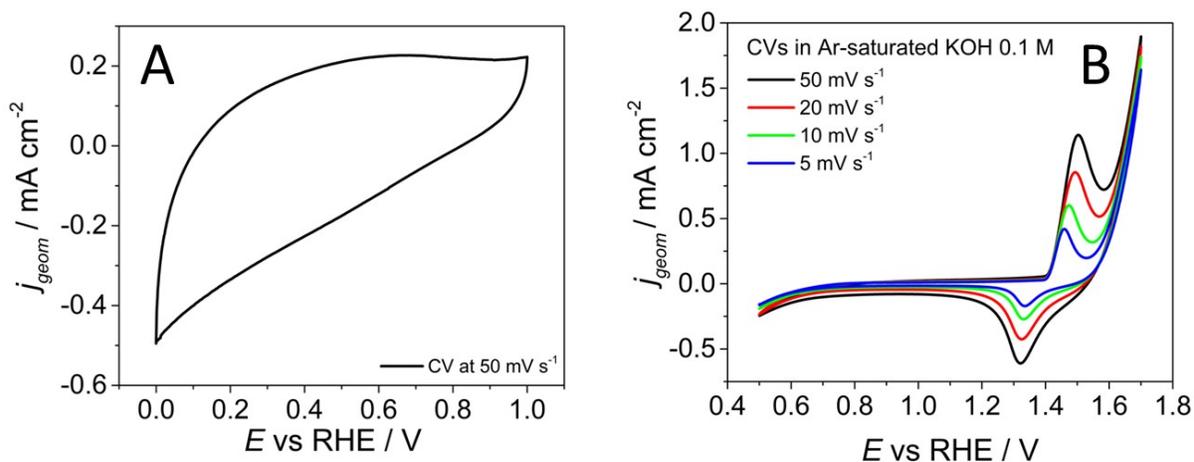


Fig. S2. (A) CV of Ni-CTF^{ph} at 50 mV s⁻¹ in Ar-saturated KOH 0.1 M solution and in a narrow range of potentials. (B) CVs of Ni-CTF^{ph} in Ar-saturated KOH 0.1 M at different scanning speed: 50 mV s⁻¹ (black), 20 mV s⁻¹ (red), 10 mV s⁻¹ (green) and 5 mV s⁻¹ (blue) and in the 0.4-1.8 range of potentials vs. RHE. Potentials were corrected for the ohmic drop taking into consideration the resistance of the system (pH = 13), while the current intensity was normalized for the geometric area of the electrode (j_{geom}).

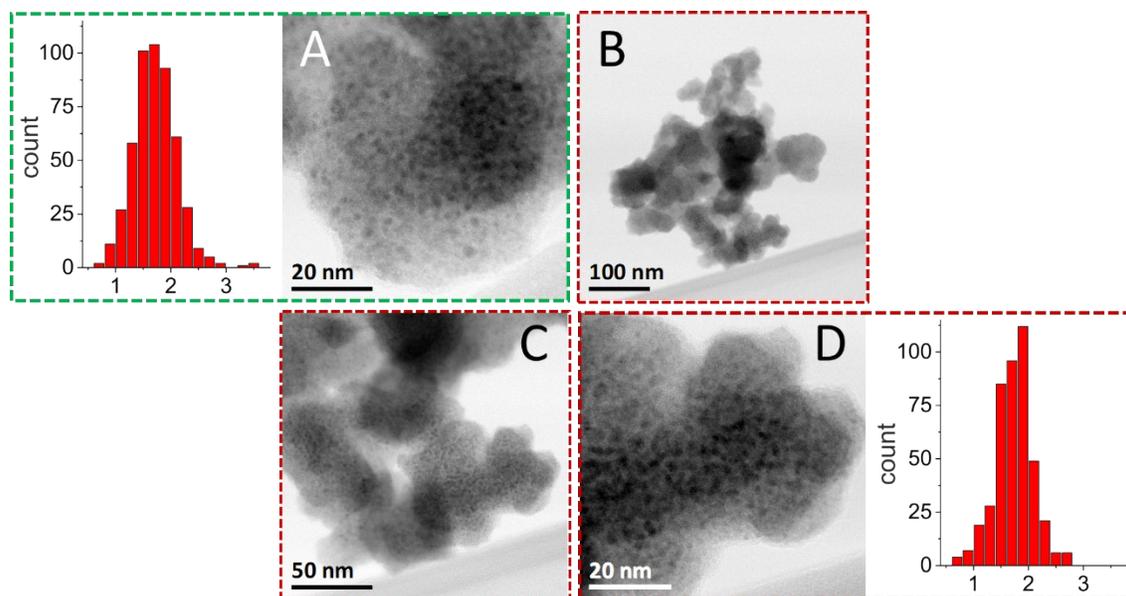


Fig. S3. HR-TEM images of the freshly prepared Ni/CTF^{ph} (1) and its used counterpart at different magnifications. Red histograms refer to the nickel particle size distribution as measured over more than 100 NPs on both pristine and used samples.

Supporting Information

References

1. M. Moro, G. Tuci, A. Rossin, C. Salvatici, E. Verlato, C. Evangelisti, F. Paolucci, G. Valenti, Y. Liu and G. Giambastiani, An ad-hoc Pyrolyzed Phoenix-like Covalent Triazine Framework for the Selective CO₂-to-Formate Electroreduction, *ACS Mater. Lett.*, 2024, **6**, 583-589. DOI: 10.1021/acsmaterialslett.3c01316