A Phoenix-like Covalent Triazine Framework as a Selective CO$_2$-to-Formate Electrocatalyst

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Significance and Relevance

We present the first example of an N-doped C-nanoarchitecture from the CTF series as a metal-free catalyst for the almost chemoselective electrochemical CO$_2$-to-HCOOH reduction (FE$_{HCOOH}$ = 66%) already under moderate reducing potentials (− 0.4 V *vs*. RHE).

Preferred and 2nd choice for the topic: Catalysis to electrify the chemical production or CO$_2$ utilization and recycling

Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) **Oral preferred or Short Oral or Poster**

Introduction and Motivations

The contribution unveils the silent electrochemical potentiality of a CTF sample already known as only moderately active in the CO$_2$-to-CO electroreduction.[1] As a modern *Phoenix*,[2] the mythological bird that regenerates from its own ashes, the CTF sample described demonstrates the impact that pyrolysis conditions have on the ultimate chemical, electronic, and morphological properties of these complex materials, giving rise to a robust catalyst with superior CO2RR selectivity toward the almost-exclusive formic acid production , at low overpotential values in an aqueous electrolyte (FE$_{HCOOH}$ as high as 66% at − 0.4 V *vs*. RHE).

[1] Zhu, X.; Tian, C.; Wu, H.; He, Y.; He, L.; Wang, H.; Zhuang, X.; Liu, H.; Xia, C.; Dai, S. Pyrolyzed Triazine-Based Nanoporous Frameworks Enable Electrochemical CO2 Reduction in Water. *ACS Appl. Mater. Interfaces* **2018**, *10*, 43588-43594.
[2] Burton, M. The myth of the Phoenix. *J. R. Soc. Arts* **1961**, *109*, 382-386.

Materials and Methods

The CTF sample of the study was prepared under classical ionothermal conditions according to literature procedures. In brief, 1,3-dicyanobenzene (mDCB) was mixed in a dry-box with an excess of anhydrous ZnCl$_2$ (5 eq.) and transferred in a quartz ampule. After drying under vacuum for 3 h, the ampule was flame-sealed and heated in a furnace (10 h at 400 °C + 10 h at 600 °C). After cooling down to r.t., the ampule was carefully opened (caution: the ampule is under pressure) and the recovered black monolith crushed and submitted to sequential washing cycles (water, HCl 1M, NaOH 1M, water and THF) before being dried to constant weight (91 % yield).

Results and Discussion

We present a rare example of an N-doped C-nanoarchitecture from the CTF series as a metal-free catalyst for the almost chemoselective electrochemical CO$_2$-to-HCOOH reduction already under moderate reducing potentials (−0.4 V vs. RHE), corresponding to a faradic efficiency (FE$_{HCOOH}$) as high as 66% (**Figure 1**). The study highlights the impact of ionothermal conditions on the electronic and morphological properties of the final CTF sample. As a modern "Phoenix", the pyrolyzed CTF described in this contribution regenerates from its ashes and transforms what is generally recognized as a moderately active CO_2-to-CO electrocatalyst in a unique and robust CTF with superior CO2RR selectivity toward the challenging CO_2-to-HCOOH electroreduction. In contrast with the general perception of pyrolysis for nanocarbon synthesis as highly batch-dependent procedures, the described protocol has unveiled an exceptionally high extent of reproducibility in terms of CTF electrochemical performance. Although any conclusion on the role of doping and material morphology, with respect to the prevalent CO_2-to-HCOOH $2e^-$ reduction path, remains speculative, it can be postulated that the presence of a high density of "chemically accessible" basic sites favors the generation of a positive CO_2 concentration gradient at the catalyst surface. At the same time, electron-poor C-sites ($C^{\delta+}$) neighboring heteroelements foster an end-on activation of CO_2 molecules through their more electron-rich oxygen atoms ($O^{\delta-}$). Thus, CO_2 undergoes a first proton-electron transfer with the generation and stabilization of the *OCHO species as the formic acid precursor.[1]

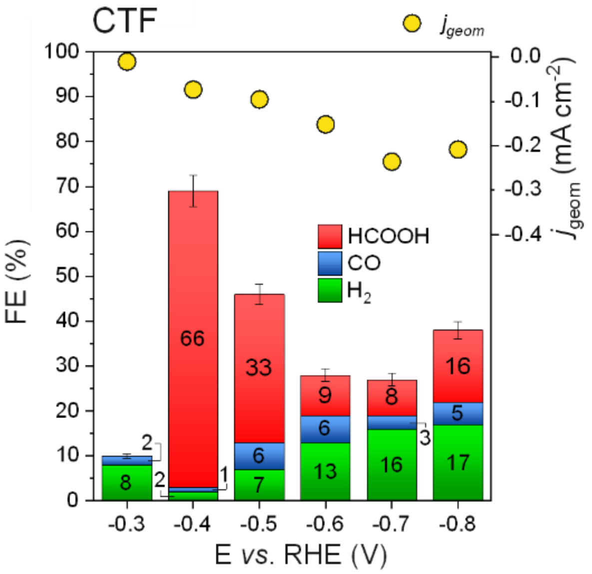

Figure 1. Faradaic Efficiency (FE_{HCOOH} - red, FE_{CO} - blue, FE_{H2} - green) and total (jgeom - yellow dots) current density values measured for the plain (metal-free) CTF in the -0.3 ÷ -0.8 V potential range vs. RHE.

The metal-free electrocatalyst doping with a Nickel active phase in the form of small-sized $Ni^0@Ni^{2+/3+}$ core-shell-like nanoparticles (NPs) leads to speculation on the synergistic or exclusive action of the two potentially active species in CO2RR (N-doped C-network *vs.* Ni NPs). The role of nickel species in promoting the CO_2-to-HCOOH electroreduction (where the plain CTF carrier failed) has also been unveiled.[2] The comparative study will also be discussed.

References

1. M. Moro, G. Tuci, A. Rossin, C. Salvatici, E. Verlato, C. Evangelisti, F. Paolucci, G. Valenti, Y. Liu, and G. Giambastiani, *ACS Materials Lett.* **2024**, 6, 583-589.
2. G. Tuci, M. Moro, A. Rossin, C. Evangelisti, L. Poggini, M. Etzi, E. Verlato, F. Paolucci, Y. Liu, G. Valenti and G. Giambastiani, *Nanoscale*, *asap*

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