**INNOVATIVE METAL FUNCTIONALIZED HYDROXYAPATITE/CARBON NITRIDE NANOCOMPOSITE MATERIAL TO ENHANCE $CO_2$ ELECTROREDUCTION TO FORMATE**

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## Significance and Relevance

This study introduces novel and functional materials for producing value-added compounds via the electrochemical reduction of $CO_2$ ($CO_2$-ER). Furthermore, recent findings highlight hydroxyapatite ($Ca_5(PO_4)_3OH$, HAP) as a key modifier able to shift the product distribution[1], directing $CO_2$ER selectivity towards formate production[2]. We present here, efficient electrocatalysts based on metal onto carbon nitride-hydroxyapatite (CN-HAP) composites. These advanced materials exhibit exceptional performance in $CO_2$-ER, underscoring their significant potential for $CO_2$ conversion technologies.

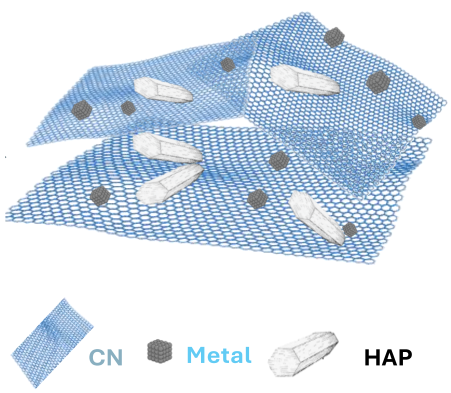
*Preferred and 2nd choice for the topic:* 1) $CO_2$ utilization and recycling 2) Advanced process with electrocatalysis and plasma utilization.
*Preferred presentation*: Oral preferred

## Introduction and Motivations

$CO_2$ as low-cost and abundant carbon resource can be used to produce high-value chemicals or fuel of high energy density: selective $CO_2$ electrochemical reduction is one of the most technologically and challenging pathways for carbon dioxide conversion. However, decreasing overpotential and enhancing both current density and faradaic efficiency (FE) remain a significant challenge, particularly in aqueous media, due to the competitive presence of hydrogen evolution reaction (HER). In this work, innovative nanocomposites comprising graphitic carbon nitride (CN), and decorated with copper (Cu) or bismuth (Bi) nanoparticles, along with hydroxyapatite (HAP) nanorods, were explored as electrocatalysts for $CO_2$ reduction to formate.

## Materials and Methods

Composite preparation consisted of one-pot synthesis of a covalent organic framework of melamine followed by thermal annealing under inert condition[3] (Fig. 1). Structural, morphological and surface properties of composites have been characterized by XRF, XPS, XRD and HRTEM.



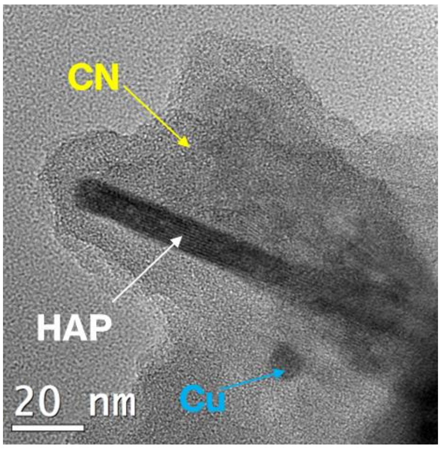




**Figure 1 Schematic representation of hydroxyapatite-carbon nitride composite material functionalized with metal nanoparticles (left), Representative HRTEM images of the HAP_Cu@CN catalyst (right).**

The performance of the electrocatalysts with copper and bismuth in $CO_2$-ER were evaluated and carried out using a three-electrode cell in a 0.1 M $KHCO_3$ aqueous solution.

## Results and Discussion

Chronoamperometric tests at different applied potentials revealed that the metal-doped HAP-based catalysts facilitate $CO_2$ER at lower overpotentials, attributed to the synergistic effect of

hydroxyapatite and metal active sites. Linear sweep voltammetry curves (LSV) showed that admixing with HAP resulted in a slight increase in system activity as the current delivered is higher in the ternary composite material. Despite the inevitable presence of the parasitic hydrogen evolution reaction (HER), the composite materials show $CO_2$ER activity. Notably, both catalysts achieved high Faradaic efficiencies for formic acid: 60% for Cu and 85% for Bi at an applied voltage of -1.0 V (*vs* RHE), with moderate current densities of 120 and 75 mA cm$^{-2}$, respectively (Fig. 2).
The catalytic behavior varied between the metals: Bi-based catalysts showed a higher preference for producing formate, whereas Cu-based catalysts exhibited greater current densities, leading to improved overall $CO_2$ conversion. Both HAP_Cu@CN and HAP_Bi@CN catalysts outperformed their unmodified binary counterparts, Bi@CN and Cu@CN, which lacked HAP. This indicates that incorporating HAP significantly enhances the activity for $CO_2$ electroreduction. Current investigations are focused on understanding the role of HAP, particularly its interactions with $CO_{2(aq)}$ and $HCO_3^-$, which are recognized as key species in the $CO_2$ reduction reaction.
In summary, both composite materials demonstrated encouraging $CO_2$ conversion rates, indicating that integrating various surfaces, such as inorganic modifiers, can lead to the development of more effective and selective electrocatalysts. These findings pave the way for future research into optimizing composite catalysts for $CO_2$ER to achieve higher efficiency and product selectivity.

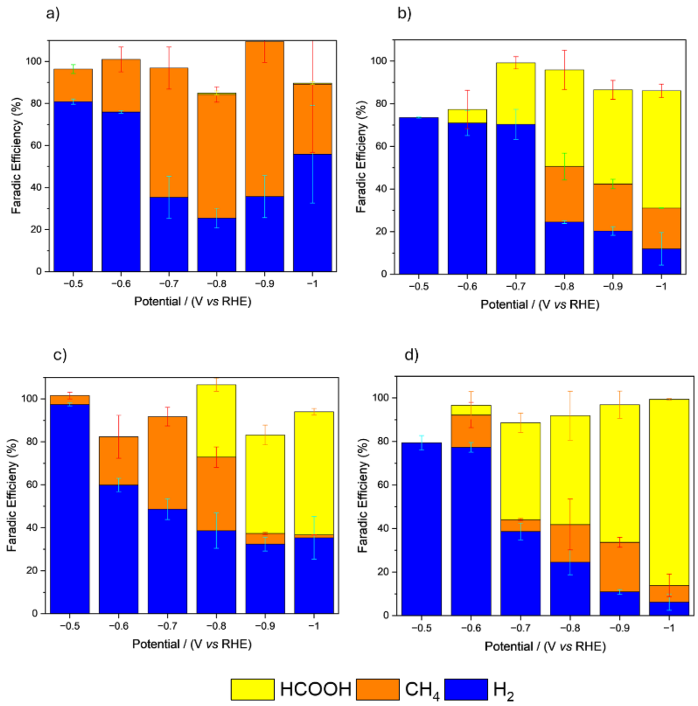



**Figure 2 Faradic Efficiency (FE) and total current density on a) Cu@CN, b) Bi@CN, c) HAP_Cu@CN, d) HAP_Bi@CN in $CO_2$ saturated 0.1 M $KHCO_3$ solution for chronoamperometric catalytic test (1 h, RT).**

## References

1. Bigica, M.; Ghiara, G.; Cristiani, P.; Campisi, S.; Gervasini, A. Interface Properties of Hydroxyapatite in Ternary Composites Cathodes for Electromethanogenesis. *New Journal of Chemistry* **2024**, *48* (22), 9909–9919. https://doi.org/10.1039/D4NJ01053A.
2. Jiao, J.; Kang, X.; Yang, J.; Jia, S.; Peng, Y.; Liu, S.; Chen, C.; Xing, X.; He, M.; Wu, H.; Han, B. Steering the Reaction Pathway of CO2 Electroreduction by Tuning the Coordination Number of Copper Catalysts. *J Am Chem Soc* **2024**, *146*, 15917–15925. https://doi.org/10.1021/JACS.4C02607/ASSET/IMAGES/LARGE/JA4C02607_0005.JPEG.
3. Gao, T.; Kumar, K. S.; Yan, Z.; Marinova, M.; Trentesaux, M.; Amin, M. A.; Szunerits, S.; Zhou, Y.; Martin-Diaconescu, V.; Paul, S.; Boukherroub, R.; Ordomsky, V. Covalent Organic Framework Derived Synthesis of Ru Embedded in Carbon Nitride for Hydrogen and Oxygen Evolution Reactions. *J Mater Chem A Mater* **2023**, *11* (36), 19338–19348. https://doi.org/10.1039/D3TA01362F.

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