Copper catalysts: bimetallic nanoparticles and single atoms for CO_2 electroreduction

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Presented in 2025, Grupo de Conversión de Combustibles, Instituto de Carboquímica (ICB-CSIC), 50018 Zaragoza.

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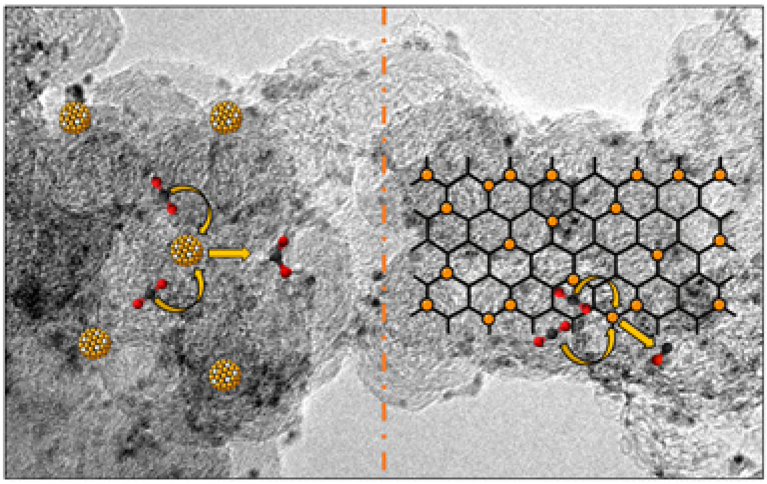
Objectives and novelty

Electrochemical CO_2 conversion offers a promising route to valorise carbon dioxide into industrially relevant products using electricity, potentially from renewable sources, thereby contributing to the defossilisation of the economy. However, unlocking its full potential requires overcoming several challenges in the CO_2 reduction reaction (CO_2RR), such as high overpotentials, competition with hydrogen evolution reaction (HER), and the intrinsic challenge of controlling selectivity across competing parallel reaction pathways. In this context, the development of active and selective catalysts is crucial for advancing this technology.

This PhD Thesis explores the development of innovative Cu-based catalysts for CO_2RR. Two specific types of catalysts were developed: bimetallic CuPt nanoparticles supported on carbon materials (CuPt/C), and copper single atoms embedded in a nitrogen doped carbon xerogel matrix (Cu-N-CXG). The CuPt/C catalysts combine the unique ability of copper to produce a broad range of CO_2RR products with the capability of platinum to reduce the reaction overpotential and modulate product selectivity, while carbon supports with tailored textural properties enhance nanoparticle distribution and facilitate mass transport. Alternatively, Cu-N-CXG catalysts exploit the maximised utilisation of copper, while nitrogen doping promotes the formation of well defined Cu-N_4 active sites and enhances the electronic properties of the carbon matrix.

In both catalytic systems, this PhD Thesis contributes to advancing the understanding of CO_2RR mechanisms and identifying key factors that govern their catalytic performance, such as the nature of the active sites, particle size, bimetallic composition, and the role of carbonaceous materials. To support this analysis, a variety of physicochemical and electrochemical characterisation techniques was employed to evaluate the structural, morphological, and catalytic properties of the synthesised materials. Among them, the use of the rotating ring disc electrode (RRDE) technique provided a novel analytical perspective to CO_2RR studies, enabling real time detection of reaction products, even at low production rates, with results consistent with those obtained by gas chromatography.



Results

Regarding the bimetallic CuPt/C catalysts, the synthesis protocol developed in this PhD Thesis enabled a homogeneous distribution of alloyed CuPt nanoparticles on different carbon supports, with platinum predominantly located at the surface. The pH of the buffer solution employed during nanoparticle synthesis was found to significantly influence the nanoparticle size. Moreover, the Cu:Pt ratio played a decisive role in modulating selectivity. Low Pt loadings, such as Cu:Pt atomic ratios of 99:1 or 95:5, enhanced the formate production at mild potentials (around -0.6 V vs. RHE) by promoting *H adsorption. However, at more negative potentials or higher Pt contents, CO reduction route is promoted, driven by the strong *CO binding ability of platinum. The influence of the carbon support was also evaluated by comparing the same CuPt/C catalyst type (95:5 ratio) supported on four different carbon materials: reduced graphene oxide (RGO), ordered mesoporous carbon (OMC), carbon xerogel (CXG), and Vulcan XC 72R. Among them, CXG exhibited a high surface area that enabled active site accessibility, along with an optimally balanced micro- and mesoporous structure that facilitated efficient diffusion of reactants and products. Overall, both the compositional tuning and support engineering emerged as key design parameters to enhance CO_2RR performance in CuPt/C catalysts.

Regarding Cu-N-CXG catalysts, composed of atomically dispersed copper embedded in nitrogen doped carbon xerogels, their synthesis involved tuning the copper precursor, the nominal Cu content, and a final acid leaching and thermal treatment step, applied only to selected samples. Catalysts subjected to this post treatment showed no detectable Cu nanoparticles −except for the sample with the highest nominal Cu content (2 wt.%)− and XAS analysis confirmed the predominance of atomically dispersed Cu-N_4 active sites in these materials.

The electrocatalytic behaviour of the samples was analysed in a three electrode set up using a RRDE as the working electrode. A specific calibration procedure was developed by bubbling controlled CO/H_2 mixtures into CO_2-saturated electrolyte and recording cyclic voltammograms at the Pt ring. These voltammograms displayed characteristic oxidation peaks whose position and intensity varied with the mixture composition. By plotting I_{peak}-E_{peak} at different CO and H_2 concentrations, a two-dimensional calibration mesh was created, enabling the identification of CO and H_2 concentrations in the electrolyte. By comparing the I_{peak}-E_{peak} values of oxidation peaks recorded at the Pt ring while applying a given potential to the catalyst at the disc, this methodology enabled the simultaneous detection of CO and H_2 produced during CO_2RR.

The Cu-N-CXG catalysts produced mainly CO/H_2 mixtures, with CO prevailing at moderate potentials (-0.6 to -0.8 V vs. RHE) and H_2 becoming dominant at more negative values. CO selectivity was associated with both the presence of Cu-N_4 active sites and the absence of residual Cu nanoparticles. Additionally, a comparative analysis of the carbon matrices confirmed that the nitrogen functionalities −especially pyrrolic/pyridonic and quaternary− also contribute to CO_2RR activity. However, the presence of Cu-N_4 coordination sites in Cu-N-CXG catalysts remains essential for effectively promoting CO formation.

Conclusions

This PhD Thesis presents the development of Cu based catalysts for electrochemical CO_2 reduction, including both CuPt/C nanoparticles and single atom Cu-N-CXG materials. In general, the results obtained highlight the importance of optimising the synergy between metal active sites and the carbon matrix to enhance performance. Furthermore, the rotating ring disc electrode (RRDE) technique was implemented as an innovative method for real time detection of CO_2RR products. These findings emphasise the value of optimal catalyst design and the use of innovative analytical methods to support the development of next generation CO_2 catalysts.

Related publications

Pérez-Rodríguez, S., Gutiérrez-Roa, M., et al. (2024). *Single atom Cu-N-C catalysts for the electro reduction of CO_2 to CO assessed by rotating ring-disc electrode*. Journal of Energy Chemistry, 88, 169 182, doi.org/10.1016/j.jechem.2023.09.005.

Gutiérrez-Roa, M. et al. (2025). *Tuning the activity and selectivity of CuPt/C catalysts for the electrochemical CO_2 reduction*. Journal of CO_2 Utilization, 95, 103084, doi.org/10.1016/j.jcou.2025.103084.

This PhD Thesis can be downloaded from:
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