Improvement of the electrocatalytic activity in sustainable energy systems based on surface modification of carbon materials

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Objectives and novelty

Water splitting, when powered by renewable energy, offers a sustainable route to produce hydrogen as fuel. The process involves two half reactions: the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. While HER is relatively fast, OER is kinetically sluggish due to its complex four-electron transfer mechanism, making it the main bottleneck for efficient hydrogen production. Overcoming these limitations requires the development of highly active, durable and cost-efficient electrocatalysts. For noble-metal-based systems, reducing the metal loading without compromising performance is an important challenge, while in the case of non-noble transition-metal catalysts, simple preparation routes that ensure high dispersion and activity are essential. Catalyst supports play a critical role in addressing these challenges, as they can enhance the dispersion of active sites, prevent particle agglomeration, improve conductivity, and even provide synergistic contributions to catalytic activity. Graphene-based materials are particularly attractive supports due to their high surface area, excellent conductivity, and tuneable chemistry. However, their conventional production from graphite via top-down routes faces limitations, as natural graphite is a limited resource with heterogeneous geographical availability, motivating the exploration of alternative, more sustainable carbon sources.

The objective of this thesis is to develop new preparation routes for OER catalysts that address the specific challenges of each system: reducing noble-metal content while preserving performance and designing simple and effective synthesis strategies for non-noble catalysts to achieve optimal dispersion and activity. To this end, carbon supports based on graphene-related materials will be employed, obtained both from graphite and from alternative carbon precursors derived from industrial wastes, integrating advances in catalyst synthesis with greener material processing.

Results

This doctoral thesis explored the preparation of active electrocatalysts for the oxygen evolution reaction through three distinct approaches, involving the use of various precursors for the development of graphene-based support materials and the different synthesis techniques for the supported catalysts.

The first approach employs industrial coke-derived graphene materials as supports for Ir-based catalysts. Despite its heterogeneous nature and high ash content, this coke-like waste can be effectively transformed into graphene oxide (GO), exhibiting a similar morphology to that obtained from commercial graphite, although its surface presents more defects and a higher degree of oxidation. Monoatomic Ir species stabilized by N-heterocyclic carbene (NHC) ligands were anchored in situ onto the graphene surface via covalent bonding to the Csp2 network, enabling direct preparation on the electrode (Figure 1). A two-step route involving initial electrografting of aniline-imidazolium salts, followed by a chemical reaction with an Ir(I) precursor yielded electrocatalysts with enhanced activity and stability compared to a direct route. Notably, Ir(I)-based electrocatalysts supported on reduced graphene oxide (rGO) from industrial waste achieved a maximum current of 33mA cm^{-2}, surpassing that of catalysts supported on rGO derived from standard graphite.

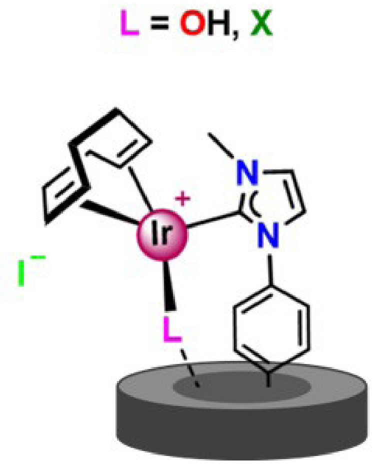

Figure 1. Structure of Ir-NHC complex supported on reduced graphene oxide.

The second strategy focuses on non-noble transition-metal electrocatalysts, specifically Ni-Fe systems prepared by electrodeposition on carbon paper modified with rGO. Here, the graphene oxide was produced from chemical oxidation and exfoliation of biochar derived from the agar-agar industry, obtained through pyrolysis at 1000 °C. Prior to chemical oxidation, the biochar underwent acidic and basic treatments to remove organic material and metallic ashes. Importantly, the graphene oxide obtained from biochar exhibits a higher nitrogen content than that obtained from graphite. This nitrogen was demonstrated to be thermally stable and integrated into the graphene structure. Electrochemical testing in alkaline media showed that Ni-Fe catalysts prepared on rGO derived from biochar exhibit higher activity, as evidenced by lower overpotentials (Figure 2, solid red curve), compared to the catalyst prepared on rGO derived from commercial graphite (solid blue curve). This enhanced activity can likely be attributed to the presence of nitrogen, highlighting a beneficial effect of the support on the OER performance.

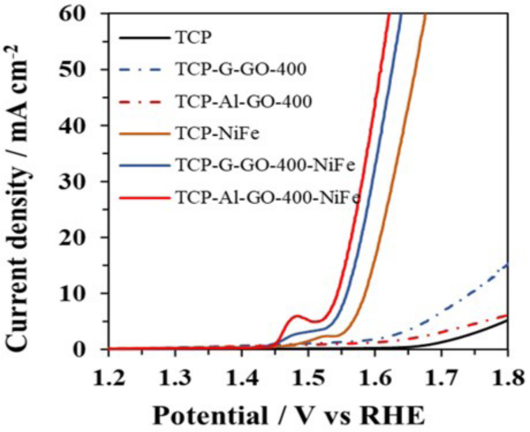

Figure 2. Linear sweep voltammograms of the different electrodes prepared in this work, recorded at 10 mV s^{-1} in the potential range of 1.2-1.8 V vs RHE in KOH 1 M.

The third approach introduces a novel route to achieve ultradispersed Ni nanoparticles in graphene aerogels. Large-flake graphene oxide suspensions obtained via the Tour method using natural graphite were mixed with Ni precursors, freeze-cast, lyophilized, and thermally reduced to form lightweight 3D networks with very low Ni loading (from 2.5 to 10 wt.%), as can be seen in Figure 3. One of the GO-Ni precursor mixtures was also processed via tape-casting into a film for comparison, revealing that the aerogel exhibits superior OER activity, likely due to better nanoparticle dispersion and smaller particle size. Furthermore, the aerogels displayed exceptional sensitivity to Fe impurities in the electrolyte, with activity enhancements upon Fe incorporation far exceeding previously reported values, making them ideal candidates for in situ characterization studies of Fe incorporation in Ni-based systems.

Conclusions

In conclusion, this doctoral research provides a comprehensive contribution to the design, synthesis and optimization of carbon-supported electrocatalyst for sustainable energy applications, particularly the oxygen evolution reaction. By exploring both conventional graphite and industrial wastes as precursors, and by developing tailored synthesis and surface modification strategies, the study demonstrated how the preparation routes and specific material properties directly influence the performance and stability of supported catalysts. Notably, this work included both noble and non-noble catalysts, addressing some of the key challenges in supported catalytic systems.

Beyond the materials themselves, the research contributes valuable methodologies, characterization, and experimental studies that link catalyst activity to the properties of the developed electrocatalysts. In this way, the findings of this thesis can support ongoing and future research on sustainable energy catalysts from multiple perspectives.

Acknowledgments

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Related publications

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[2] González-Ingelmo, M., Granda, M., Ruiz, B., Fuente, E., Sierra, U., Rocha, V.G., González, Z., Álvarez, P., Menéndez, R. Proactive Effect of Algae-Based Graphene Support on the Oxygen Evolution Reaction Electrocatalytic Activity of NiFe. Materials, 16(24), (2023) 7641.

[3] González-Ingelmo, M., López García, M., Oropeza, F.E., Álvarez, P., Blanco, C., Santamaría, R., Rocha, V.G. Ultra-high dispersion of Ni-based OER catalysts on graphene 3D networks enhances the in situ Fe3+ catalytic activation. Journal of Materials Chemistry A, 11(44), (2023) 24248.

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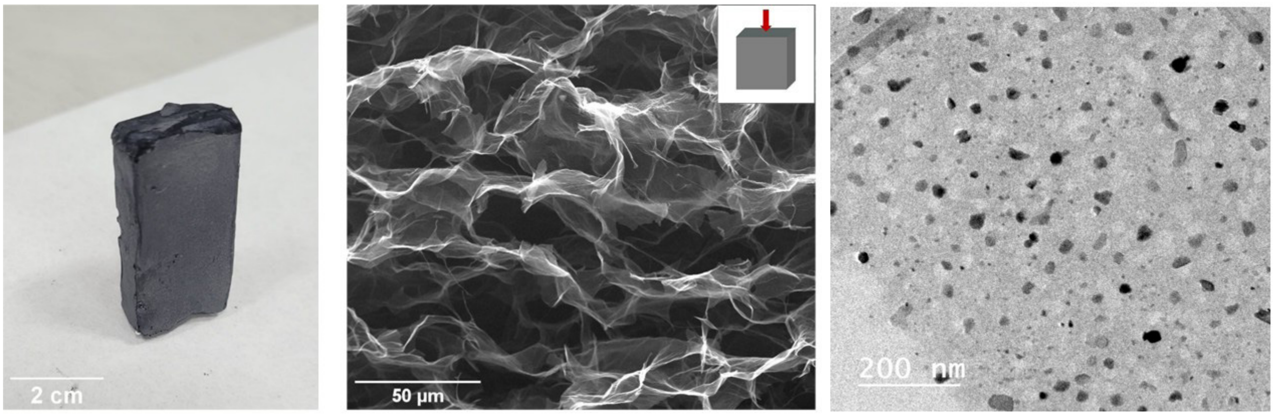

Figure 3. Macroscopic aspect, SEM and TEM images of Ni-doped graphene aerogels (from left to right)