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INDICE

Editorial

Empezamos el curso con energías renovadas tras el merecido descanso estival, y lo hacemos con el Boletín número 77 del Grupo Español del Carbón, que llega cargado de contenidos.

Abrimos este número con una entrevista al profesor Juan Matos Lale, de la Universidad Autónoma de Chile, referente internacional en fotocatálisis y materiales de carbono. Su trayectoria, marcada por la cooperación científica entre Europa y Latinoamérica, nos ofrece una visión enriquecedora sobre los retos actuales en investigación y sostenibilidad.

En la sección "Conociendo a Nuevos Grupos", contamos con la contribución del Grupo de Catálisis y Materiales de la Facultad de Ciencias y Tecnologías Químicas de la Universidad de Castilla-La Mancha. En su trabajo se presenta el uso de borocarbonitruros derivados de grafeno como electrocatalizadores para la producción de hidrógeno en medio alcalino.

Este número recoge además varias reseñas de tesis doctorales: Alberto Martínez Jódar, Sara Payá González, María González-Ingelmo y Daniel Fernández Carrasco, del INCAR-CSIC; y de Víctor Calvo Peña y Manuel Gutiérrez Roa, del ICB-CSIC.

No podemos dejar de celebrar el merecido reconocimiento al Profesor Diego Cazorla-Amorós (Universidad de Alicante), galardonado con el prestigioso premio de la *European Carbon Association*. Su labor investigadora y su compromiso con la comunidad científica internacional son motivo de orgullo para todos los que formamos parte del GEC.

Asimismo, compartimos la crónica del congreso internacional *The World Conference on Carbon-CARBON 2025*, celebrado en Saint-Malo (Francia), donde la delegación española tuvo una participación destacada, tanto en el plano científico como en el social.

Desde el equipo editorial, agradecemos a todos los autores que han hecho posible este número. Os animamos, como siempre, a seguir compartiendo vuestros avances, ideas y proyectos en este espacio común que es el Boletín del GEC.

¡Nos vemos pronto en Zaragoza en la XVII Reunión del GEC!

José Luis Pinilla Ibarz
Juana María Rosas

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Entrevistamos a...

En este número del Boletín tenemos el placer de entrevistar al profesor Juan Matos Lale de la Universidad Autónoma de Chile.

¿Qué le llevó a realizar un Doctorado en Física y Química de Superficie centrado en los materiales de carbono y su aplicación en fotocatálisis y energía solar? ¿Siempre había tenido claro que quería dedicarse a la investigación en materiales?

Hace algo más de 30 años, cuando estaba haciendo mi tesis de pregrado en Lic. Química, trabajaba con catalizadores a base de Ni y Mo soportado en carbonos porosos, que, en esa época, nadie los llamaba aun así. Mi tema de tesis se centraba en reacciones de hidrotratamiento en refino de petróleo, y en especial en reacciones de hidrogenación de olefinas. Buena parte de los pretratamientos que realizábamos tenían que ver con procesos de sulfuración de los catalizadores, para simular las fases activas sulfuradas, principalmente MoS_2 por su enorme actividad en procesos de hidrodesulfuración. Una tesis de este tipo genera desgaste por la enorme carga de contaminación que se generaba, además de generar malestares de salud. Sin embargo, al mismo tiempo, descubrí que una nueva área de la catálisis llamada fotocatálisis, estaba creciendo remarcablemente. Al buscar información por simple curiosidad, descubrí que tan sólo había dos artículos publicados donde los autores intentaba mejorar la fotoactividad del TiO_2 empleando soportes catalíticos, y en estos, sólo uno incluía un carbón activado. Sorprendido quedé al ver sólo el carbono funcionaba eficientemente y los otros soportes clásicos inhibían al TiO_2. Así nació mi proyecto de tesis doctoral el cual propuse a mi tutor en el Instituto Venezolano de Investigaciones Científicas (IVIC) y luego, uno de los grandes maestros de la fotocatálisis, el Prof. Jean-Marie Herrmann me aceptó en la Ecole Centrale de Lyon (ECL), y así comenzó este viaje.

Su doctorado se llevó a cabo dentro del Programa de Cooperación de Posgrado Franco-Venezolano entre la Escuela Central de Lyon y el Instituto Venezolano de Investigación Científica, además, fue Director de la Red Franco-Chilena de Valorización de Biochar para su Aplicación en Energía y Remediación Ambiental entre 2017 y 2020. ¿Cuáles han sido (y son) sus lazos profesionales con Francia?

Así es, como mencionaba antes, el Prof. Herrmann me aceptó para ser su discípulo en la ECL a través de ese programa, siendo el primer doctor de Venezuela y quizás el primero de América Latina graduado en esa temática de investigación. Posteriormente, lideré junto a mi colega y amiga, la Dra. Conchi O. Ania, del Laboratorio CEMHTI (Extreme Conditions and Materials: High Temperature and Irradiation, CNRS-Université de Orleáns), la Red Franco-Chilena de Valorización de Biochar para su Aplicación en Energía y Remediación Ambiental, la cual aún se mantiene a través de diversos proyectos que me encuentro ejecutando con dicha investigadora, así como con el Prof. Jean-Marc Chovelón, y Corinne Ferronato del IRCELYON (Institute of Research on Catalysis and the Environment of Lyon).

¿Cuáles, a su juicio, son los principales retos para fortalecer la colaboración científica entre la Unión Europea y Latinoamérica?

El tema de producción y almacenamiento de energía aun cuando no está 100 % resuelto, está bastante adelantando y se espera que en los próximos 10 años, pueda estar casi agotado. Sin embargo, nuevas formas de energía siempre son bien valoradas y bienvenidas. Sin embargo, aún a pesar de los enormes esfuerzos de la comunidad internacional, el tema de remediación ambiental, no sólo de agua y aire contaminados, si no más grave aún, la contaminación de suelos agrícolas, son los temas de mayor relevancia que nos permitiría avanzar enormemente en lo que hemos llamado Aseguramiento Alimentario. Agua, Aire y Suelo sanos para el Aseguramiento de Alimentos.

¿En qué líneas de investigación se centra en estos últimos años la actividad del grupo que dirige en la Universidad de Autónoma de Chile, Group of Smart Nanomateriales?

Actualmente dirijo mi investigación hacia temas relacionados con la remediación ambiental, materiales de construcción inteligentes, y fotosíntesis artificial.

¿Cuál sería el descubrimiento que le gustaría hacer en los próximos años dentro del campo de la Ciencia de Materiales basados en carbono?

Sería un honor diseñar, construir, e implementar un material totalmente sostenible y sustentable que permita resolver varios problemas a la vez relacionados con las áreas antes indicadas. Me interesa sobremanera que la gente de escasos recursos pueda tener acceso a viviendas dignas, de alta calidad energética, así como sustentables. Diseñar materiales fotoactivos en el rango visible del espectro solar, que sean eficientes, económicos, sustentables, y sobre todo multifuncionales, permitiría bajar costes en la producción de paneles de construcción. Igualmente incorporar estos elementos en la propia cadena de mantenimiento de las viviendas, remediando eficiente y dinámicamente el agua doméstica y generando espacios limpios, es la meta trazada.

Con relación a los campos de la foto- y electrocatálisis, así como en la producción de energía limpia ¿Cree que durante la última década los materiales de carbono han adquirido más protagonismo? ¿O, por el contrario, cree que pierden algo de terreno a favor de otros tipos materiales?

En lo absoluto. De más de 1 millón de artículos publicados en los últimos 60 años sobre diversas formas de materiales de carbono, más del 80 % se han publicado en las últimas 2 décadas. Los nanocarbonos han sido, son y serán los materiales por excelencia.

Actualmente, usted es Director de la Asociación Chilena de Materiales de Carbono, y además, contribuyó a fundar la Federación Latinoamericana de Carbono, siendo su Presidente entre los años 2016 y 2018. Desde estas posiciones, ¿Cómo describiría el grado de integración y cooperación de los países Latinoamericanos en términos de investigación? ¿Cómo cree que podría aumentarse y mejorarse dicha colaboración?

Históricamente, hemos mantenido diversas colaboraciones que nos han permitido avanzar de forma constante y muy eficientemente en diversas áreas de investigación, principalmente también gracias al apoyo de investigadores españoles que han hecho posible esta integración. Debo mencionar el apoyo que recibimos en Latinoamérica entre 1980 y el 2010 de profesores como Avelino Corma, Francisco Rodríguez-Reinoso, Enrique Rodríguez-Castellón, José Rivera, Francisco Carrasco-Marín, Ángel Linares, Carlos Moreno-Castilla y muchos otros, que a partir del 2010 han colaborado cada vez más con los grupos de Latinoamérica, donde nuestra mayor limitante ha sido y es, históricamente, el presupuesto limitado para investigación de punta, lo que evidentemente ha incidido en una menor integración de nuestros países.

Por último, ¿Cuándo tendremos el placer de verlo por España?

Pues, este año, a finales del mes de octubre, he sido invitado a dar una Keynote en la VI Conferencia Internacional sobre Ciencia e Ingeniería Avanzada de Polímeros en Tenerife, por lo que pronto estaré por casa, aunque casi todos los años voy a España.

Graphene-derived borocarbonitrides as electrocatalysts for hydrogen production in alkaline media

Borocarbonitruros derivados de grafeno como electrocatalizadores para la producción de hidrógeno en medio alcalino

J. Cencerrero[1], A. Romero[2], A. de Lucas-Consuegra[1], A.R. de la Osa[1], P. Sánchez[1*]

Department of Chemical Engineering. University of Castilla-La Mancha, Avda. Camilo José Cela 12, 13071, Ciudad Real, Spain.

[1] Faculty of Chemical Sciences and Technologies,

[2] Technical School of Agronomic Engineers.

** paula.sanchez@uclm.es*

Abtract

In the context of sustainable electrochemical hydrogen production, metal-free carbon-based materials are emerging as scalable and versatile alternatives. Graphene-derived materials, in particular, stand out due to their high electrical conductivity and tunable properties for specific applications. This work presents borocarbonitrides as efficient electrocatalysts for the hydrogen evolution reaction (HER) under alkaline conditions due to their remarkable stability across a wide pH range. Optimizing synthetic parameters such as calcination temperature and time revealed that 900 °C and 10 h produced the most favorable conditions, providing a high surface area, enhanced reduction, and improved crystallinity. XPS analyses confirmed a high degree of homogeneity on B-C-N surfaces, the restoration of graphene aromaticity, and a significant presence of graphitic nitrogen. Additionally, the boric acid/urea ratio was studied as a critical variable, and the optimal performance was obtained at a ratio of 0.5:40. The most active electrocatalyst exhibited excellent stability under high current density conditions (12 h and 1,000 LSV cycles) and achieved electrochemical activation with an η_{10} of 295 mV.

Resumen

Ante la necesidad de producción electroquímica sostenible de hidrógeno verde, los materiales carbonosos sin metal emergen como una alternativa prometedora por su escalabilidad y versatilidad. Entre ellos, los derivados del grafeno destacan por su elevada conductividad eléctrica y la posibilidad de ajustar sus propiedades a distintas aplicaciones. En este trabajo, se presentan los borocarbonitruros como electrocatalizadores eficientes para la reacción de evolución de hidrógeno (HER) en medio alcalino, gracias a su notable estabilidad en un amplio rango de pH. Para su síntesis, se optimizaron parámetros como la temperatura y el tiempo de calcinación, observándose que las condiciones de 900 °C y 10 h proporcionan una mayor área superficial, mayor grado de reducción y mejor cristalinidad. Los análisis de XPS confirmaron una elevada homogeneidad en las superficies B-C-N, con restauración de la aromaticidad del grafeno y una presencia significativa de nitrógeno grafítico. Asimismo, se evaluó la relación ácido bórico/urea como variable crítica, identificándose un valor óptimo de 0,5:40. El electrocatalizador más activo mostró excelente estabilidad bajo altas densidades de corriente (12 h y 1000 ciclos LSV), alcanzando una activación electroquímica con un η_{10} de 295 mV.

1. Introduction

As conventional energy sources become depleted, clean energy alternatives such as hydrogen conversion devices are gaining attention. Electrochemical water splitting has emerged as a promising technology due to its environmental compatibility, high energy efficiency, and broad applicability [1]. The most advanced electrocatalysts for water splitting are based on noble metals (Pt, Ru, Ir), but their scarcity and high cost limit its large-scale use [2]. Consequently, the search for metal-free electrocatalysts has attracted significant interest.

Graphene-based materials stand out within carbon metal-free catalysts because of their high carrier mobility, chemical stability, and large surface area, which enhance water-splitting efficiency [3]. However, their zero band gap restricts electrochemical activity, requiring heteroatom doping (N, B, S, P) to tailor their electronic properties [4]. Previous studies highlight that dual-doping with B and N can activate adjacent carbon atoms within the carbon matrix through electron restructuring, thereby enhancing HER performance [5]. Additionally, each heteroatom leads to specific semiconductor properties to the material [6]. In this context, borocarbonitrides (BCNs) derived from graphene represent a tunable class of materials with excellent optical, electrical, and thermal properties, achievable by adjusting the B, C, and N ratios [7]. Therefore, determining the optimal proportion of each heteroatom in the electrocatalyst is crucial for maximizing its efficiency in HER applications. Furthermore, the wide range of stoichiometric combinations attainable from elemental composition precursors allows for the synthesis of different BCN compositions (Figure 1). The structural tunability of these compositions directly manage their physicochemical properties, which consequently affects their suitability for specific catalytic and functional applications. Incorporation of B-C and N-C bonds modifies electron density, narrows the band

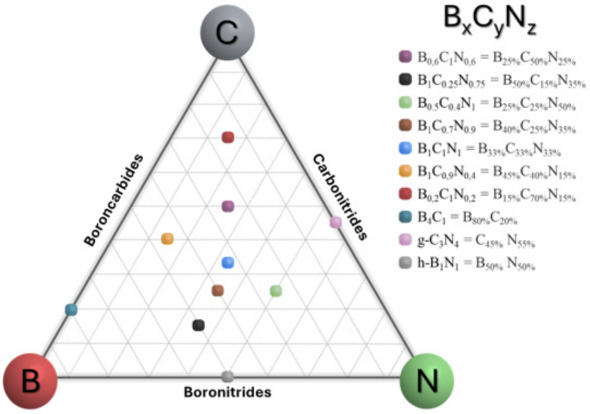

Figure 1. Ternary phase diagram of the BxCyNz materials [9]
Figura 1. Diagrama de fase ternario de los materiales BxCyNz

gap, and introduces lattice polarization, significantly improving electrocatalytic performance [4]. The BCN character in particular leads to a high degree of miscibility between similarly sized atoms, which results in polarization in the carbon skeleton due to the different electronegativity, which in turn leads to an excellent electrochemical property [8].

Although the hydrogen evolution reaction (HER) is commonly studied in acidic media, alkaline conditions provide advantages for industrial scaling, such as higher operating current densities, lower membrane costs, and easier electrode fabrication [10]. However, HER in alkaline electrolytes is kinetically slower due to the need for water dissociation prior to hydrogen formation [11]. Thus, catalytic activity depends on efficient H-OH bond cleavage and stabilization of H* intermediates [12]. In BCNs, N-doping facilitates water adsorption and electron activation through its lone pair, while boron, acting as a weak Lewis acid, generates p-type domains that further enhance HER activity [13]. As nitrogen is a weak Lewis base, it can attract H_2O molecules to the proton orbitals. In addition, it has been reported that the free pair on the N atom can activate the π-electrons of carbon for the reduction reaction, and the doubly doped carbon matrix has a much deeper function [14].

This work reports the electrochemical performance of BCNs synthesized under different conditions, aiming to establish an efficient and scalable metal-free electrocatalyst for alkaline HER (1 M KOH). The process relies on a simple one-pot synthesis with non-toxic reagents, using graphene-based precursors as the carbon source, which represents the main novelty of this study. Key parameters such as calcination temperature (700-900 °C), time (2-12 h), and boric acid/urea molar ratio (0.5:40-2:40) were systematically optimized, leading to enhanced properties and stable high-current operation comparable to commercial 20% Pt/C.

2. Experimental

Figure 2 illustrates a scheme of the synthesis method. A mixture of graphite oxide (GrO), boric acid (BA), and urea was dissolved in deionized water under sonication to ensure the solubility of BA. Detailed experimental synthesis was published elsewhere [9]. Subsequently, the solvent was evaporated at 80 °C and stirred at 400 rpm. The resulting slurry was then transferred into a quartz boat and heated in a horizontal tubular furnace at different temperatures and times (heating rate of 4 °C min^{-1}) under a N_2 atmosphere (flow rate: 50 mL min^{-1}). The BCN obtained was further homogenised using a mortar and pestle. Synthesized samples were denoted as X-Y-BCN, where X represented the calcination temperature (700, 800, and 900 °C) and Y represented the calcination time (2, 6, 10, and 12 hours). Samples denoted as BC, synthesized using precursors of C and B, and CN, synthesized using precursors of C and N, were generated as comparative purpose. Finally, to evaluate the impact of the heteroatom ratio on electrochemical activity, various syntheses were conducted by varying the BA/urea molar ratio used as precursors (ranging from 0.5:40 to 4:40), while maintaining constant the total moles of doping agent (mmol BA + mmol urea = 82 mmol). The resulting samples were designated as x-BCN, where x represented the BA/urea molar ratio.

3. Results

3.1. Influence of calcination temperature

The morphological characteristics of the obtained materials are presented in SEM images of Figure 3, which displays typical graphene-based materials [15]. Figure 3a illustrates the graphene sheets in graphite oxide (GrO) that exhibit slight separation, more so than in graphite. Upon pyrolysis of GrO using boron and nitrogen as reducing agents, the graphene sheets undergo corrugation and develop porosity (displayed in the image itself), facts that intensify with increasing calcination temperature.

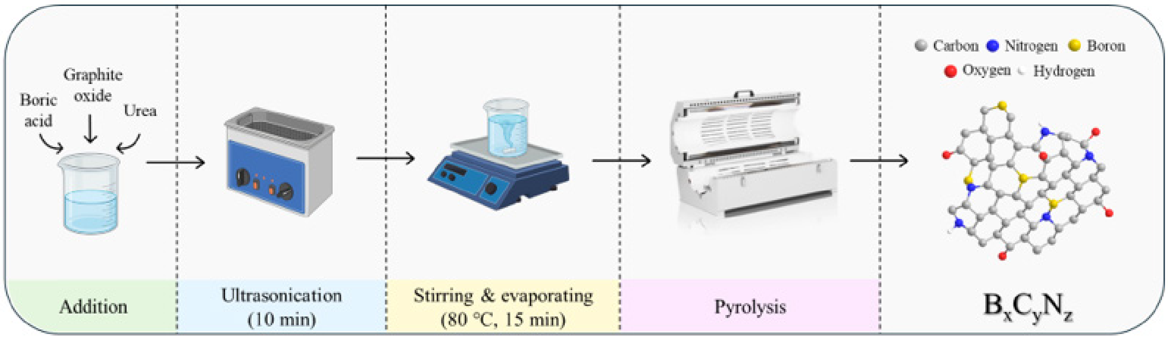

Figure 2. Scheme of BCN synthesis
Figura 2. Esquema de la síntesis de **BCN**

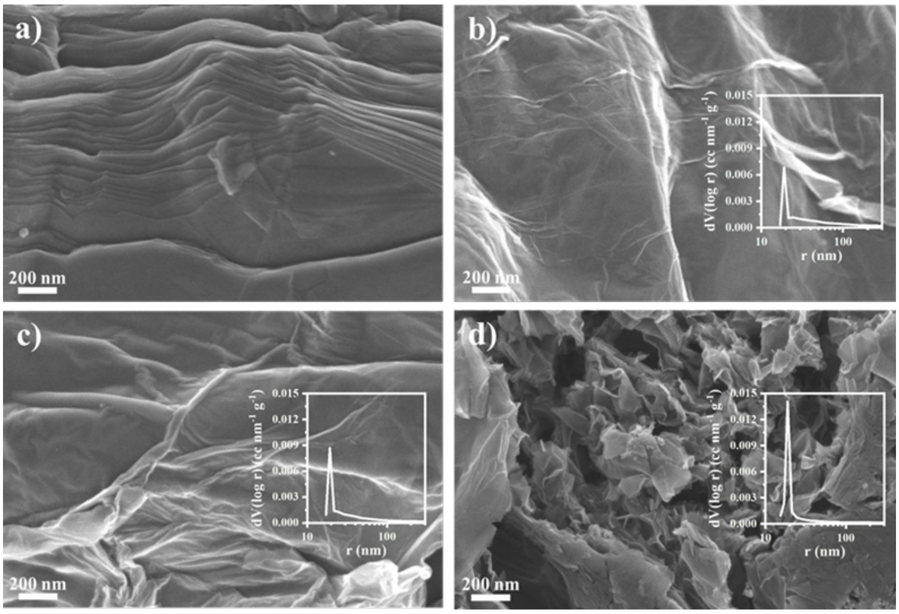

Figure 3. SEM images of a) GrO and b) 700-10h-BCN, c) 800-10h-BCN and d) 900-10h-BCN, including its pore size distribution.
Figura 3. Imágenes SEM de a) GrO y b)700-10h-BCN, c) 800-10h-BCN y d) 900-10h-BCN, incluyendo sus distribuciones de tamaño de poro.

B1s and N1s spectra obtained from the high-resolution XPS for the BCNs are showed in Figure 4, illustrating how the bonds B-N and Graphitic-N rise and Pyridinic-N (N1) drop along the temperature increase. The formation of the B-N bond restores the lost aromaticity of the graphene surface, which was lost when defects were created by introducing heteroatoms, as conjugated 6-unit rings are regenerated [16]. This fact, along with the electronic semiconductor effects (p and n) introduced by both heteroatoms, may improve the electronic properties [17]. Furthermore, the increase in Graphitic-N and the decrease in Pyridinic-N, attributed to the higher stability of Graphitic-N at elevated temperatures [18], have been confirmed to result in higher currents in HER [14].

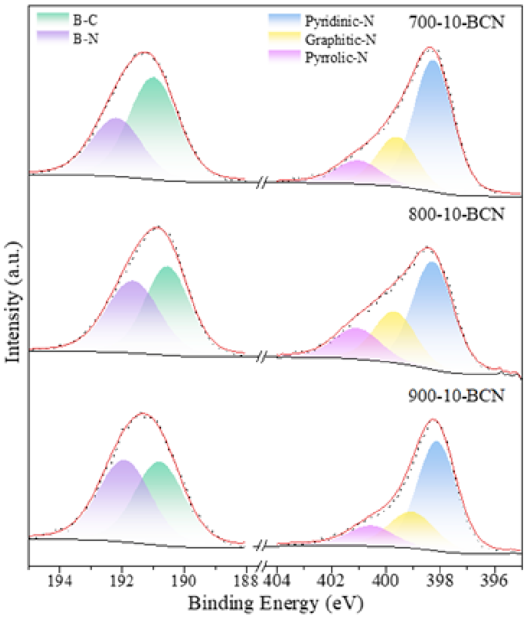

Figure 4. High-resolution core level B1s and N1s XPS spectra of BCN calcined at different temperatures.
Figura 4. Espectros XPS de alta resolución de B1s y N1s de BCN calcinado a diferentes temperaturas.

To evaluate the electrocatalytic performance of the synthesized BCNs, Figure 5a presents the corresponding LSVs in comparison to commercial 20% Pt/C. Due to achieve better physicochemical parameters, 900-10-BCN became the most active catalyst with an overpotential at -10 mA cm^{-2} (η_{10}) of 380 mV. It can be seen in Figure 5b that the B-N bond and surface area has a direct influence on the η_{10} of the electrocatalyst calcined at different temperatures. Apart of obtaining a high amount of Graphitic-N and low oxidated groups in the surface, the BCN with higher values of BN bond and surface area (BCN calcined at 900 °C), reached lower η_{10}.

3.2. Influence of the calcination time

Once the calcination temperature is set at 900 °C, it is crucial to optimize the calcination duration to obtain an ideal BCN structure characterized by stability and enhanced electrical properties. The calcination times tested ranged from 2 to 12 hours, and the resulting textural and electrochemical properties of the BCNs are presented in Table 1. This table evidenced with the decreased in surface area that the extending the calcination beyond 10 hours appears to reduce the porosity initially generated. Due to the carbon-based nature of the BCNs, prolonged calcination times lead to structural collapse [19], so that pore volume and surface area decrease after 12 h at 900 ºC (900-12-BCN) compared to those calcined for 10 h. Additionally, no substantial changes in the crystallinity of the samples were observed with longer calcination times, except for a slight increase in the LC parameter. The optimal structural characteristics of BCNs obtained at 10 h of calcination allowed it to achieve the best electrochemical performance with a η_{10} of 380 mV.

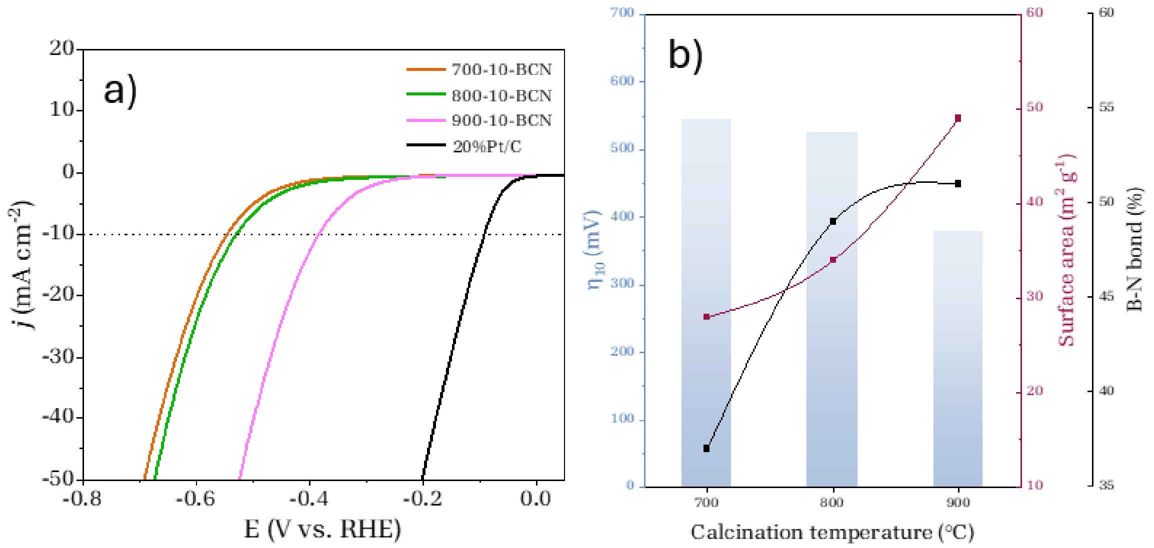

Figure 5. a) Linear Sweep Voltammetry, b) the corresponding Tafel plots, and c) η_{10} and surface area vs. calcination temperature of BCNs calcined at different temperatures.

Figura 5. a) Voltametría de Barrido Lineal, b) y sus correspondientes gráficos de Tafel, y c) η_{10} y área superficial vs. Temperatura de calcinación de los BCNs calcinados a diferentes temperaturas.

Table 1. Textural and electrochemical properties of the BCNs calcined at 900 °C for different calcination times.

Tabla 1. Propiedades texturales y electroquímicas de los BCN calcinados a 900 °C durante diferentes tiempos de calcinación.

Samples	Total pore volume (cm^3 g^{-1})	Surface area (m^2 g^{-1})	XRD L_A (nm)	XRD L_C (nm)	η_{10} (mV)
900-2-BCN	0.092	22	5.3	3.5	590
900-6-BCN	0.097	36	6.5	3.6	460
900-10-BCN	0.200	49	6.7	5.0	380
900-12-BCN	0.124	40	6.7	5.1	505

3.3. Influence of the B:N molar ratio

As previously mentioned, the ratio B:N may strongly affect to electrochemical properties of BCNs. Several changes are produced on the porosity of the material when the ratio B:N are varied (Table 2). The higher addition of B the lower material porosity, generating decreases its area and total pore volume. This may be due to many B atoms are not fixed in the carbon matrix and they are filling the pores [19], so the calcination should be more severe in these materials to release and create porosity. It can be seen that with the addition of a low amount of B (0.5:40-BCN and 1:40-BCN) generated the highest textural properties of BCNs obtained (total pore volume, surface area and crystallinity). As expected, 0.5:40-BCN and 1:40-BCN obtained the highest electrochemical performance (η_{10} of 380 mV), but it is selected 0.5:40-BCN due to its better activity under high voltages.

Table 2. Crystallographic parameters and textural properties of the BCN synthesized.

Tabla 2. Parámetros cristalográficos y propiedades texturales del BCN sintetizado.

Samples	Total pore volume (cm^3 g^{-1})	Surface area (m^2 g^{-1})	XRD L_A (nm)	XRD L_C (nm)	η_{10} (mV)
BC	0.010	11	-	-	540
CN	0.155	43	5.4	3.7	390
0.5:40-BCN	0.205	51	6.7	4.8	380
1:40-BCN	0.200	49	6.7	5	380
2:40-BCN	0.110	32	5.4	3.1	410
4:40-BCN	0.060	20	4.5	2.9	520

To further explore the stability and activation at various current densities ranging from 10 to 50 mA cm^{-2}, a chronopotentiometric (CP) test was conducted (Figure 6). For comparison, the performance of the CN catalyst was also evaluated under identical conditions. At the beginning of the CP test at -10 mA cm^{-2}, the voltage for the 0.5:40-BCN gradually increases to -0.36 V over 2 h. Upon increasing the current densities to -20, -30 and -50 mA cm-2, the voltage decreases accordingly and it keeps activating the material, reaching -0.40, -0.42 and -0.46 V, respectively. The material was activated reaching 0.295 and 0.350 mV upon returning the current density to -10 and -20 mA cm^{-2}, respectively, and it keeps on activating. This η_{10} of 295 mV achieved promising HER performance in 1 M KOH, which is similar to metal-based electrocatalysts described in the literature [20–23]. In contrast, the CN catalyst did not achieve the high activity obtained with 0.5:40-BCN, which is attributed to the absence of HER promotion of the B-doping in the carbon matrix.

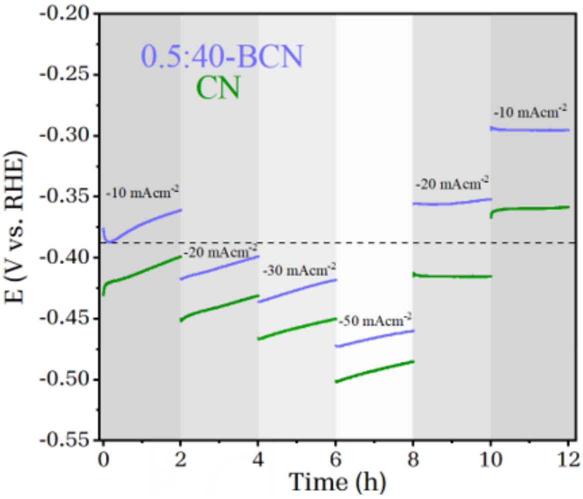

Figure 6. CP curves recorded at different current densities of CN and 0.5:40-BCN.
Figura 6. Curvas CP registradas a diferentes densidades de corriente de CN y 0,5:40-BCN.

4. Conclusions

Promising metal-free borocarbonitrides based on graphite oxide as carbon matrix were successfully synthesized via one-step pyrolysis. The temperature and time calcination were critical in order to improve the electrocatalytic activity in alkaline HER, obtaining 10 hours and 900 °C as optimal conditions of calcination. These synthetic conditions generated a low oxygen content and a stable graphene-like structure doped with B and N. In-depth XPS analysis revealed the strong N-B bond formed during the calcination, allowing the creation of a stable and homogeneous B-C-N ternary material. The ratio of B:N were optimized obtaining for a ratio 0.5:40-BCN the most active catalyst. This catalyst reached η_{10} = 295 mV in 1 M KOH after an activation under LSVs and chronopotentiometry, which is close to that observed for a commercial 20% Pt/C catalyst.

5. Acknowledgements

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6. References

[1] T. Qiu, J. Cheng, Z. Liang, H. Tabassum, J. Shi, Y. Tang, W. Guo, L. Zheng, S. Gao, S. Xu, R. Zou, Unveiling the nanoalloying modulation on hydrogen evolution activity of ruthenium-based electrocatalysts encapsulated by B/N co-doped graphitic nanotubes, Appl Catal B 2022; 316:121626.

[2] W. Zhang, H. Lou, G. Yang, 2D Metal-Free BSi5 with an Intrinsic Metallicity and Remarkable HER Activity, Journal of Physical Chemistry Letters 2023; 14:11036-11042.

[3] M. Cai, L. Xu, J. Guo, X. Yang, X. He, P. Hu, Recent advances in metal-free electrocatalysts for the hydrogen evolution reaction, J Mater Chem A Mater 2024; 12:592-612.

[4] J.B. Matsoso, C. Journet, N.J. Coville, Z. Sofer, Co-doping Graphene with B and N Heteroatoms for Application in Energy Conversion and Storage Devices, ChemNanoMat 2022; 8:e202200134.

[5] M. Zhou, X. Jiang, W. Kong, H. Li, F. Lu, X. Zhou, Y. Zhang, Synergistic Effect of Dual-Doped Carbon on Mo2C Nanocrystals Facilitates Alkaline Hydrogen Evolution, Nanomicro Lett 2023; 15:1–11.

[6] J. Lin, P. Guan, Polymeric nitrogen in alkaline earth metal N-rich nitrides (MN2, M = Be, Mg, Ca, Sr, and Ba): A first-principles study, Comput Mater Sci 2023; 229:112427.

[7] H. Tabassum, R. Zou, A. Mahmood, Z. Liang, S. Guo, A catalyst-free synthesis of B, N co-doped graphene nanostructures with tunable dimensions as highly efficient metal free dual electrocatalysts, J Mater Chem A Mater 2016; 4:16469-16475.

[8] L. Ci, L. Song, C. Jin, D. Jariwala, D. Wu, Y. Li, A. Srivastava, Z.F. Wang, K. Storr, L. Balicas, F. Liu, P.M. Ajayan, Atomic layers of hybridized boron nitride and graphene domains, Nature Materials 2010; 9(5): 430–435.

[9] J. Cencerrero, P. Sánchez, A. de Lucas-Consuegra, A.R. de la Osa, A. Romero, Metal-free borocarbonitrides as electrocatalysts for the hydrogen evolution reaction under alkaline media, Journal of Electroanalytical Chemistry 2025; 977:118856.

[10] T. Wu, M. Sun, H.H. Wong, C.H. Chan, L. Lu, Q. Lu, B. Chen, B. Huang, Recent advances and strategies of electrocatalysts for large current density industrial hydrogen evolution reaction, Inorg Chem Front 2023; 10:4632–4649.

[11] D. Strmcnik, M. Uchimura, C. Wang, R. Subbaraman, N. Danilovic, D. Van Der Vliet, A.P. Paulikas, V.R. Stamenkovic, N.M. Markovic, Improving the hydrogen oxidation reaction rate by promotion of hydroxyl adsorption, Nature Chemistry 2013; 5(4):300-306.

[12] W. Ma, X. Zhang, W. Li, M. Jiao, L. Zhang, R. Ma, Z. Zhou, Advanced Pt-based electrocatalysts for the hydrogen evolution reaction in alkaline medium, Nanoscale 2023; 15:11759-11776.

[13] D. Shi, B. Chang, Z. Ai, H. Jiang, F. Chen, Y. Shao, J. Shen, Y. Wu, X. Hao, Boron carbonitride with tunable B/N Lewis acid/base sites for enhanced electrocatalytic overall water splitting, Nanoscale 2021; 13:2849-2854.

[14] J. Cencerrero, A. Romero, A. de Lucas-Consuegra, A.R. de la Osa, P. Sánchez, Towards metal-free nitrogen-doped graphene aerogels as efficient electrocatalysts in hydrogen evolution reaction, FlatChem 2023; 42:100554.

[15] Y. Kang, Z. Chu, D. Zhang, G. Li, Z. Jiang, H. Cheng, X. Li, Incorporate boron and nitrogen into graphene to make BCN hybrid nanosheets with enhanced microwave absorbing properties, Carbon N Y 2013; 61:200-208.

[16] L. Qu, Z. Zhang, H. Zhang, H. Zhang, S. Dong, Transformation from graphitic C3N4 to nitrogen-boron-carbon ternary nanosheets as efficient metal-free bifunctional electrocatalyst for oxygen reduction reaction and hydrogen evolution reaction, Appl Surf Sci 2018; 448:618-627.

[17] V. Todi, Investigation Of Reactively Sputtered Boron Carbon Nitride Thin Films. University of Central Florida. Doctoral Thesis 2011.

[18] C. Cheng, Y. Li, C. Maouche, B. Li, Y. Zhou, S. Wang, X. Cheng, J. Yang, Green synthesis of N, P-co doped porous reduced graphene oxide as an active metal-free electrocatalyst toward oxygen reduction reaction, Journal of Electroanalytical Chemistry 2021; 883: 115058.

[19] L. Zhang, J. Xin, K. Liu, G. Wei, D. Xiong, W. Lan, Effective transesterification of castor oil to biodiesel catalyzed by novel carbon-based calcium composite, Energy Convers Manag 2024; 307:118368.

[20] J.J. de la Cruz-Cruz, M.A. Domínguez-Crespo, E. Ramírez-Meneses, A.M. Torres-Huerta, S.B. Brachetti-Sibaja, A.E. Rodríguez-Salazar, E. Pastor, L.E. González-Sánchez, Data supporting the in situ synthesis by organometallic method of Vulcan supported PdNi nanostructures for hydrogen evolution reaction in alkaline solution, Data Brief 2022; 42:108256.

[21] B. Zhang, J. Li, Q. Song, S. Lv, Y. Shi, H. Liu, g-C3N4-modulated bifunctional SnO2@g-C3N4@SnS2 hollow nanospheres for efficient electrochemical overall water splitting, Appl Surf Sci 2022; 589:153016.

[22] A. Ahmad, A. Davarpanah, L. Thangavelu, D.O. Bokov, R.A. Alshgari, A.M. Karami, Self-assembled pine-like CuCo/CP configuration as efficient electrocatalysts toward electrochemical water splitting, J Mol Liq 2022; 351:118635.

[23] Z. Hou, H. Jiang, Y. Guo, K. Huang, F. Zhao, Y. Xu, P. Peng, S. Zou, J. Yan, J. Zhang, Enhancing acidic hydrogen evolution through pyrrolic nitrogen-doped reduced graphene oxide triggering two-electron oxygen reduction, Inorg Chem Front 2024; 11:4318-4328.

El catedrático de la UA Diego Cazorla-Amorós recibe el premio de la *European Carbon Association*

Raúl Berenguer Betrián

Universidad de Alicante

Nuestro compañero Diego Cazorla-Amorós, catedrático del Departamento de Química Inorgánica y perteneciente al Instituto de Materiales (IUMA) de la Universidad de Alicante (UA), ha sido galardonado con el prestigioso premio de la *European Carbon Association* (*ECA*) en reconocimiento a sus sobresalientes aportaciones en el campo de los materiales de carbón y a su servicio a la comunidad científica europea.

Se trata del primer científico español en lograr este galardón, que destaca su labor investigadora en la preparación y caracterización de materiales de carbón para aplicaciones en energía, protección ambiental, catálisis heterogénea, electrocatálisis, fotocatálisis, almacenamiento de gases como metano e hidrógeno, así como en el desarrollo de sensores y biosensores.

El profesor Cazorla-Amorós recogió el premio de la ECA el pasado 2 de julio durante el congreso internacional *The World Conference on Carbon 2025* que se celebró en Saint-Malo (Francia). Mediante este premio, la ECA reconoce su dedicación, innovación y liderazgo en el avance del conocimiento en materiales de carbón, así como por su compromiso con la colaboración internacional y el desarrollo tecnológico en este campo.

Los resultados de sus investigaciones se reflejan en la publicación de más de 360 artículos en revistas de alto impacto. Es coinventor de 18 patentes, ha dirigido y participado en más de un centenar de proyectos de investigación financiados tanto a nivel nacional como europeo y ha dirigido 36 tesis doctorales.

Director del grupo de investigación Materiales Carbonosos y Medio Ambiente de la UA, el profesor Cazorla-Amorós ha desempeñado varios cargos de liderazgo, incluyendo la presidencia del Grupo Español de Carbón, así como la dirección del Departamento de Química Inorgánica de la UA y del IUMA.

A lo largo de su carrera, Cazorla-Amorós ha sido investigador y profesor invitado en países como Francia, Reino Unido, Países Bajos, Estados Unidos y Japón, colaborando estrechamente con centros de excelencia internacional. Su compromiso con la comunidad científica europea es destacado. Ha impartido y participado en la organización de conferencias internacionales en numerosos eventos y ha presidido diferentes grupos de trabajo.

Además, el investigador de la UA ha liderado el desarrollo y la patente de equipos para mediciones de adsorción a alta presión y ha fundado una *startup* que distribuye estos equipos a nivel mundial en colaboración con empresas multinacionales del sector. Su grupo de investigación en la Universidad de Alicante es uno de los referentes internacionales en el área de los materiales porosos y la caracterización de sólidos mediante técnicas de adsorción de gases.

Desde el equipo editorial del Boletín de GEC aprovechamos esta ocasión para darle la enhorabuena por este reconocimiento internacional tan prestigioso.

El catedrático de la UA, Diego Cazorla Amorós, recogiendo el premio de la *European Carbon Association*.

The World Conference on Carbon (CARBON 2025) Saint-Malo – Francia

Victoria G. Rocha y Zoraida González Arias

Instituto de Ciencia y Tecnología del Carbono (INCAR-CSIC)

Entre los días 29 de junio y 4 de julio de 2025 se celebró en Saint-Malo (Francia) el congreso *“The World Conference on Carbon – CARBON 2025”*, punto de encuentro para los investigadores del campo de los materiales de carbono. Gracias a la excelente organización por parte de la *Societé Francophone dÉtude des Carbones (SFEC)* y la Universidad de Rennes (en el marco de la *European Carbon Association, ECA*), y al idílico enclave costero de esta localidad de la bretaña francesa, los numerosos participantes procedentes de 39 países disfrutaron, en plena ola de calor, no sólo de varias jornadas de ciencia de calidad sino también de espléndidos actos sociales.

Las actividades arrancaron, en las instalaciones de *Le Grand Large (Palais des Congrés)*, la tarde del domingo 29, con la recogida de las acreditaciones y el disfrute de un coctel de bienvenida exquisito y relajado, con sabor a mar y disfrutando de unas espléndidas vistas de la ciudad intramuros. Como no podía ser de otra manera, comenzaron los saludos y reencuentros con colegas a los que no veíamos hace tiempo…y allí estábamos una importante representación de españoles (gran parte de ellos socios del GEC), procedentes de diferentes centros y puntos de la geografía nacional. A la mañana siguiente tuvo lugar el arranque de la parte científica del programa, con la calurosa bienvenida de Nathalie Job (coordinadora del congreso y presidenta de la SFEC) y la primera de cinco interesantes conferencias plenarias, impartida por el Profesor Fernando Pereira (Universidad de Oporto), quien comenzó mostrando la gran diversidad de aplicaciones catalíticas de los protagonistas del evento. Este fue el punto de partida para el desarrollo de diversas sesiones paralelas en las que, a través de conferencias magistrales y comunicaciones orales, se abordaron las investigaciones más recientes tanto sobre *Kerógenos, carbon, coque, grafito, procesos de carbonización/grafitización,* así como *la síntesis, procesamiento, caracterización y modelado de materiales de C (materiales innovadores, nanomateriales),* y su posterior aplicación *en biología, medicina y seguridad; medioambiente; procesos y tecnologías electroquímicas; catálisis ; electrónica; aplicaciones estructurales y gestión térmica*.

La más que numerosa (y animada) delegación española (representada por investigadores de Asturias, Cataluña, Castilla la Mancha, País Vasco, Zaragoza, Málaga, Granada y Alicante) participó muy activamente, con varios miembros del GEC actuando como moderadores de sesiones de orales o de conferencias plenarias. Pero quizá lo más destacable fueron los trabajos presentados durante las 5 jornadas del congreso, tanto en formato de comunicaciones orales (21 contribuciones) como en formato poster (25 contribuciones).

El congreso, como cada año, ha puesto de manifiesto la versatilidad y el papel crucial de los materiales de carbono en la transición hacia un futuro más sostenible y tecnológicamente avanzado. Las temáticas abordadas ponen de manifiesto el amplio espectro de investigación en el que nos encontramos inmersos y consolidan al carbono como un actor clave en la resolución de los desafíos globales.

Uno de los pilares del congreso fue la *catálisis* y la *descarbonización*. Se destacó la importancia de adaptar la química superficial de los materiales de carbono para desarrollar soluciones catalíticas sostenibles. Entre las innovadoras estrategias presentadas se incluyó la modificación de superficies con heteroátomos como oxígeno, nitrógeno, azufre y fósforo, que contribuyen a la obtención de catalizadores eficientes para diversas aplicaciones. Entre ellas, destacó la eliminación de contaminantes del agua empleando N-CNTs, materiales altamente eficientes en dicha aplicación. Asimismo, la valorización de CO_2 a metanol, empleando en este caso MOx-CNTs como materiales activos, afianza la importancia de la investigación con el objetivo de mejorar el rendimiento catalítico y reducir las emisiones de este gas de efecto invernadero. También son numerosos los trabajos encaminados al desarrollo de catalizadores eficientes que permiten optimizar la electrólisis del agua (incluyendo el agua de mar), para la producción de hidrógeno verde.

Otro avance notable fue la presentación de catalizadores orgánicos de radical/carbono vs. reacciones de oxidación en fase gaseosa y condiciones ambientales, los cuales son capaces de inactivar virus a temperatura ambiente sin necesidad de reactivos químicos o energía externa.

El *almacenamiento de energía* fue otro de los temas que atrajo un gran número de los trabajos presentados. Fueron significativos los avances mostrados en el desarrollo de supercondensadores que emplean, como materiales activos de electrodo, desde carbonos activados de alto rendimiento hasta fibras derivadas de celulosa y posteriormente dopadas. Otro de los puntos destacados fue el estudio de la influencia de las estructuras de nanocarbono grafíticas y los grupos funcionales superficiales sobre el rendimiento de estos dispositivos electroquímicos, junto con el desarrollo de carbonos altamente porosos a partir de hidrocarbón para otras aplicaciones de almacenamiento de energía. En el ámbito de las baterías, se exploraron desde ánodos de carbono derivados de lignina para baterías de iones de litio y sodio, hasta materiales compuestos avanzados para baterías de litio-azufre, que mitigan el efecto de la disolución y migración de polisulfuros de azufre. La producción escalable de ánodos de silicio recubiertos de carbono para baterías de iones de litio mediante pirólisis de metano también puso de manifiesto el compromiso de la investigación realizada con la sostenibilidad.

En cuanto a las aplicaciones ambientales, se destacó la capacidad de los materiales de carbono para enfrentar retos significativos. Por ejemplo, se presentaron resultados muy interesantes sobre la capacidad de adsorción de azul de metileno de residuos de poda de manzana carbonizados siguiendo un método hidrotermal. Por otro lado, se resaltó tanto la superioridad de los carbones activados frente a la desulfuración del biogás, como la eficiencia de carbones activados funcionalizados para la eliminación de CO_2. En esta misma línea, las investigaciones llevadas a cabo empleando biochar modificado con calcio como material activo para la captura de CO_2 o carbonos activados enriquecidos con nitrógeno para la captura y separación de este gas de efecto invernadero evidencian el potencial de estos materiales. Igualmente, y atendiendo a la necesidad de controlar la calidad del agua, se exploró el empleo de nanotubos de carbono y de nanocarbones modificados para la eliminación de contaminantes de naturaleza orgánica. En esta misma línea se están desarrollando también diversos sensores electroquímicos a partir de diferentes nanomateriales de C para la detección de contaminantes emergentes en agua.

Finalmente, el congreso puso de relieve los avances en la *síntesis y caracterización de nuevos nanomateriales y estructuras de carbono*. En este contexto se mostraron los últimos avances en el desarrollo de nanotubos de carbono para electrónica y electroquímica, así como de grafeno en diversas formas (óxido de grafeno, grafenos reducidos, puntos cuánticos de carbono) para diversas aplicaciones.

Dentro de la programación científica, y algo que nos llenó de orgullo, nuestro compañero y catedrático de la Universidad de Alicante (UA), Diego Cazorla Amorós, recibió el prestigioso premio de la *European Carbon Association* (ECA). Sus numerosas y destacadas contribuciones en el campo de los materiales de carbono y su servicio a la comunidad científica europea han hecho posible que Diego sea el primer científico español en obtener este gran reconocimiento, por el que le damos nuestra más sincera enhorabuena.

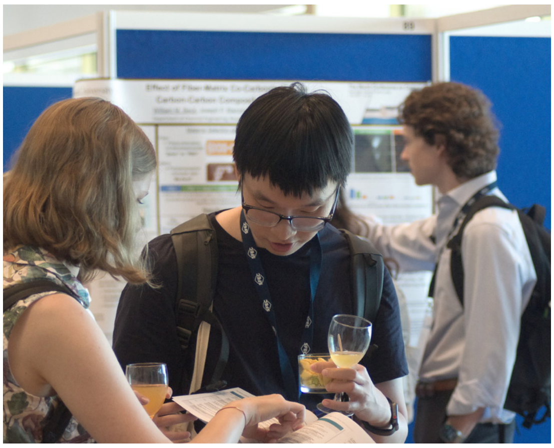
Pero no todo iban a ser charlas, posters y discusiones científicas. Estaba claro que, teniendo en cuenta el enclave en el que nos encontrábamos, había que aprovechar la oportunidad. Así que, el miércoles por la tarde, el comité organizador del congreso tenía programados varios actos sociales, entre los cuales fue bastante difícil elegir. Gran parte del grupo de españoles visitamos el Monte Saint-Michel, impresionante enclave de la región de Normandía y declarado Patrimonio Mundial de la UNESCO en 1979. Durante varias horas nos perdimos en sus calles empinadas y en su impresionante abadía desde cuyas torres pudimos disfrutar de una maravillosa vista de la bahía. Otro grupo de "valientes" se decidió por el viaje en barco que les permitió disfrutar de las vistas de Saint-Malo desde el mar. El "mareo" se vio después recompensado por una fiesta en la que disfrutaron tanto de la música como de las viandas locales.

Para dar fin a la parte social del congreso, el jueves entrada ya la tarde, y tras haber disfrutado de la excelente Conferencia Plenaria impartida por el Prof. Vincent Meunier, disfrutamos de la cena de gala organizada por nuestros colegas franceses en las propias instalaciones del Palacio de Congresos. Allí disfrutamos tanto de la cena en sí como de los fotomatones instalados (¡un éxito más de la organización!). Y el colofón, lo puso el baile que, por supuesto, estuvo más que animado y que luego unos pocos continuamos en la noche intramuros. Sinceramente, gracias por volver a hacernos disfrutar de nuestra profesión y de la ciencia que hacemos.

Ceremonia inaugural del congreso

Instalaciones del Palacio de Congresos Le Grand Large, sede del congreso

Comunicación oral impartida por Maria González Ingelmo (INCAR-CSIC)



Sesión de posters

Visita al Mount Saint Michel y paseo en barco por la costa de Saint-Malo

Delegación española

Preparation of bidimensional materials for energy storage and environmental applications

Alberto Martínez Jódar

alberto.mj@incar.csic.es

Presented in 2024, Instituto de Ciencia y Tecnología del Carbono (INCAR-CSIC).
Supervisors: Juan Ignacio Paredes Nachón (INCAR-CSIC), Silvia María Villar Rodil (INCAR-CSIC).

Objectives and novelty

In recent years, nanomaterials and more specifically two-dimensional (2D) materials have been attracting great interest due to the change in physicochemical properties from their bulk forms and the possibility of their selective modulation. Thus, 2D materials feature a wide variety of applications such as electrochemical energy storage, biomedicine, (opto) electronics, (electro)catalysis, or (bio)sensors, among others. Despite all the research efforts, there are still limitations in the preparation and modification methods of 2D materials regarding the control of both structural quality and final properties. In this context, the present doctoral thesis has mainly focused on:

(1) Optimization of top-down methodologies for the preparation of MoS_2 and $MoSe_2$ 2D nanosheets. For this purpose, sonication-assisted liquid phase exfoliation (LPE) in organic medium and an optimized cathodic electrochemical exfoliation (CEE) in both aqueous and organic medium were employed.

(2) Investigation of molecular functionalization and chalcogen vacancies generation strategies in 2D TMDs. An electrolytic methodology for covalent molecular functionalization of MoS_2 nanosheets during CEE was implemented, as well as a reductive treatment at temperature for the generation of chalcogen vacancies (S and Se, respectively) in MoS_2 and $MoSe_2$ nanosheets obtained via LPE.

(3) Applications of 2D nanosheets as catalysts for the degradation of water pollutant species and as electrodes for Li-ion electrochemical storage. The intrinsic catalytic activity of MoS_2 and $MoSe_2$ 2D nanosheets obtained by LPE (with and without chalcogen vacancy generation) was compared, and the catalytic potential of functionalized MoS_2 nanosheets was studied, respectively, towards the reduction of nitroarenes and organic dyes is aqueous medium. The performance of MoS_2 nanosheets prepared via LPE and cathodic EE in organic medium as anodes for lithium electrochemical devices was investigated.

Results

A CEE strategy in organic medium has been developed to exfoliate thin MoS_2 nanosheets for their implementation as electroactive material for anodes in lithium storage devices. While previous studies have been focused in tetraalkylammonium salts, this study explored trimethylalkylammonium salts as electrolyte for the first time. After optimizing the exfoliation experimental conditions, an electrolyte based on the hexyltrimethylammonium cation ($HTMA^+$) was chosen, as it yielded a higher degree of exfoliation, prevented the well-known 2H-1T phase transition and led to thinner MoS_2 nanosheets related to other tested electrolytes.

The performance of MoS_2 nanosheets obtained by CEE (ee-MoS_2) was compared with those obtained by LPE (lpe-MoS_2) as anodes for lithium storage devices. The smaller thickness of ee-MoS_2 nanosheets (which decreases their electrical resistance and shortens the Li diffusion paths) and their greater flexibility resulted in better electrochemical performance as an anode for Li storage compared to lpe-MoS_2, in terms of obtained gravimetric capacity during discharge, capacity retention with increasing current density (rate capability) and long-term cyclability.

Beyond energy storage, 2D TMDs also display promising applications in the field of catalysis as an alternative for noble metal-based catalysts due to their relative earth-abundance, cost-effectiveness and suitable catalytic activity towards several reactions of interest, such as hydrogen and oxygen evolution reaction, CO_2, N_2 and, more recently, several nitroarenes reduction reaction. Nonetheless, catalytic performance of 2D nanosheets is strongly dependent on their colloidal stability in the corresponding medium and, despite potential intrinsic advantages of CEE, no electrochemical functionalization method has been reported yet. To that purpose, an electrochemical functionalization method of MoS_2 nanosheets was optimized towards enhanced hydrophilicity for their use as a catalyst for the reduction of nitroarenes and organic dyes, relevant in water decontamination and in the synthesis of certain pharmaceuticals.

Specifically, the electrochemical functionalization treatment led to acetic acid-derivatized MoS_2 nanosheets displaying improved colloidal stability in water related to non-derivatized ones. External supply of electrons (from cathodic potential or chemical electron donor) enables functionalization, and the presence of S vacancies in the basal plane of the nanosheets enables the anchoring of organic functional groups. The functionalized MoS_2 nanosheets showed significantly higher catalytic activity than other MoS_2-based catalysts (1T or 2H phase) previously reported. A relationship between the order of reduction reaction and the net electric charge of the substrate molecules was found. The functionalized nanosheets maintained good catalytic efficiency at realistic concentrations of nitroarenes and in binary and ternary mixtures of such reactants. In addition, to facilitate their handling and reuse, the nanosheets could be immobilized on a polymeric support.

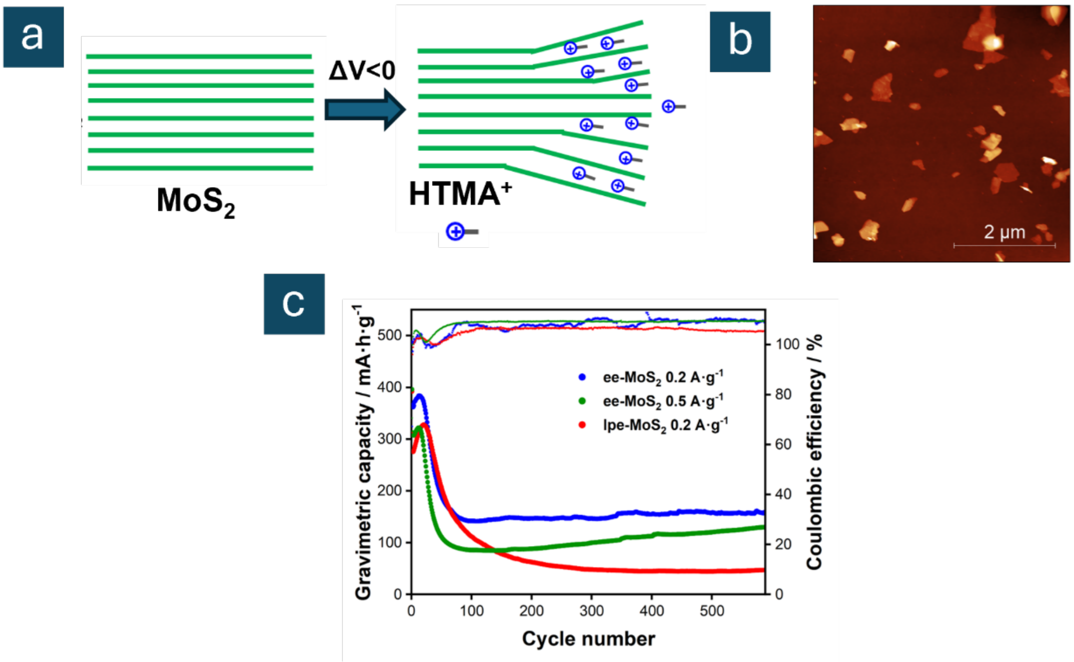
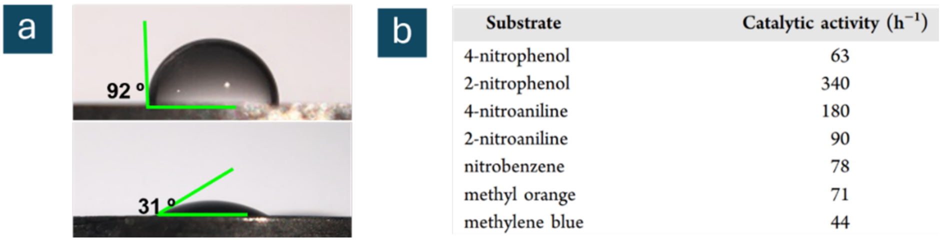


Figure 1. a) Scheme of the electrochemical intercalation mechanism during CEE with HTMA+-based electrolyte. b) Digital image obtained by atomic force microscopy of ee-MoS_2 2D nanosheets. c) Gravimetric capacity for long-term cyclability (larger circles) and coulombic efficiency (smaller circles) for ee-MoS_2 and lpe-MoS_2 nanosheets at different current densities for lithium-ion storage.



Substrate	Catalytic activity (h^{-1})
4-nitrophenol	63
2-nitrophenol	340
4-nitroaniline	180
2-nitroaniline	90
nitrobenzene	78
methyl orange	71
methylene blue	44

Figure 2. a) Contact angle with a water droplet of the non-functionalized (92º) and functionalized (31º) nanosheets. b) Catalytic activity values of the functionalized MoS_2 nanosheets with the studied substrates.

Besides, nitroarene reduction reaction is an operation of interest in water remediation and pharmacological industry. Although MoS_2 is one of the most investigated members for this purpose, other TMDs remained unexplored, and such was the case with $MoSe_2$. Thus, intrinsic catalytic activities of 2D MoS_2 and $MoSe_2$ 2D nanosheets exfoliated by LPE towards reduction of nitroarenes were compared, with a superior catalytic performance of the latter. DFT studies allowed proposing a mechanism for the reduction reaction and provided an explanation for the selectivity shown by the different nitroaniline isomers to $MoSe_2$ nanosheets during catalysis. With aim to facilitate the practical implementation of $MoSe_2$ nanosheets, those were immobilized onto a polymeric support to facilitate their reuse during several catalytic cycles, displaying an appropriate catalytic activity retention.

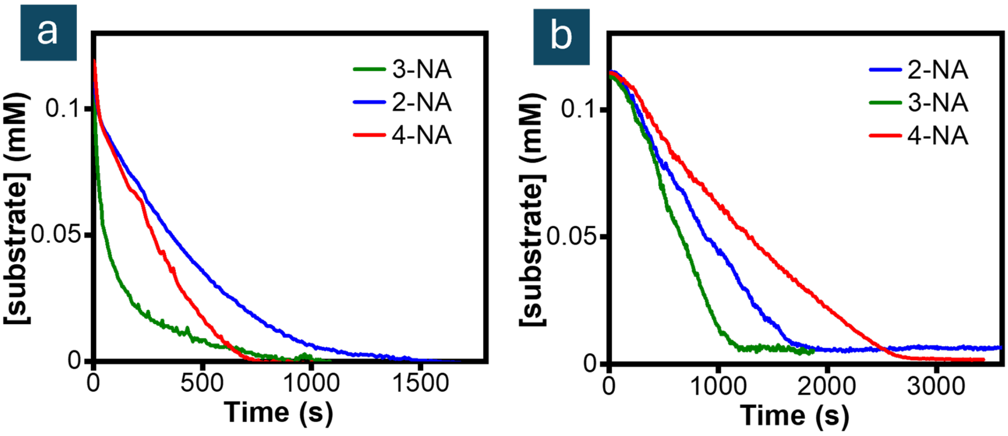


Figure 2. Kinetic profiles for the reduction reaction of several nitroaniline isomers in the presence of a) $MoSe_2$ and b) MoS_2 2D nanosheets as catalyst in aqueous solution.

Conclusions

It was verified that ee-MoS_2 nanosheets obtained by the CEE optimized methodology showed improved performance for Li-ion storage rather than LPE-MoS_2. An electrochemical functionalization method to enhance MoS_2 nanosheets colloidal stability towards their use as catalyst for nitroarene and organic dyes reduction was successfully developed. It was confirmed by both experimental and DFT calculations that $MoSe_2$ 2D nanosheets possess higher intrinsic catalytic activity than MoS_2 nanosheets for the reduction reaction of nitroarenes.

Related publications

[1] Martínez-Jodar A, Villar-Rodil S, Munuera JM, Castro-Muñiz A, Coleman JN, Raymundo-Piñeiro E, Paredes JI, Two-Dimensional MoS_2 Nanosheets Derived from Cathodic Exfoliation for Lithium Storage Applications, Nanomaterials, 2024, 14-932, 1-25.

[2] Martínez-Jódar A, Villar-Rodil S, Salvadó MA, Carrasco DF, Pertierra P, Recio JM, Paredes JI. Two-dimensional transition metal dichalcogenides beyond MoS_2 for the catalytic reduction of nitroarenes: $MoSe_2$ exhibits enhanced performance, Applied Catalysis B: Environmental, 2023, 339, 123174.

[3] García-Dalí S, Paredes JI, Villar-Rodil S, Martínez-Jódar A, Martínez-Alonso A, Tascón JMD, Molecular Functionalization of 2H-Phase MoS_2 Nanosheets via an Electrolytic Route for Enhanced Catalytic Performance, Applied Materials & Interfaces, 2021, 13, 33157-33171.

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Copper catalysts: bimetallic nanoparticles and single atoms for CO_2 electroreduction

Manuel Gutiérrez Roa

mgutierrez@icb.csic.es

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

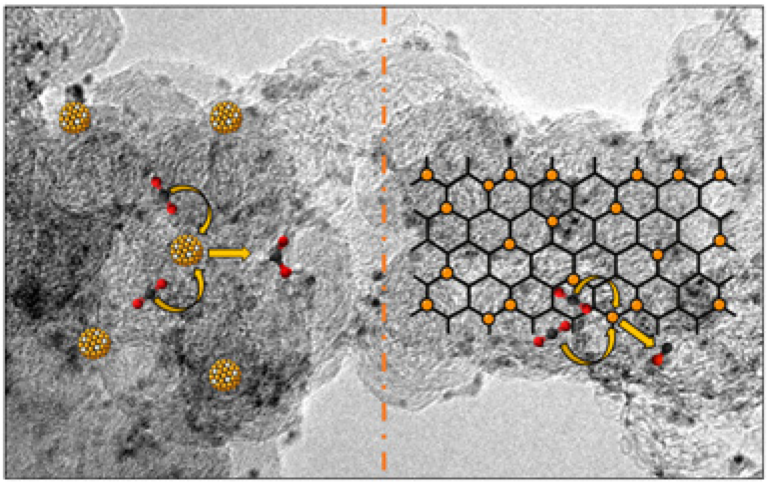
Supervisors: Dr. Sara Pérez Rodríguez (Instituto de Carboquímica-CSIC) and Dr. David Sebastián del Río (Instituto de Carboquímica-CSIC).

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.

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Synthesis and characterization of nanostructured, heteroatom-doped carbon materials for use in sodium-ion capacitors

Sara Payá González

sara.paya99@gmail.com

Presented in 2025, Instituto de Ciencia y Tecnología del Carbono (CSIC), Oviedo, Spain.

Supervisors: Dr. Marta Sevilla Solís and Dr. Noel Díez Nogués (Instituto de Ciencia y Tecnología del Carbono).

Objectives and novelty

The increasing demand for sustainable and efficient energy storage devices is one of the major challenges in the global transition towards renewable energy systems that can allow the decarbonization of our society. Lithium-ion batteries currently dominate the market, but the scarcity and uneven geographical distribution of lithium resources raise serious concerns regarding their long-term viability. In this context, sodium-ion based technologies have emerged as a cost-effective and sustainable alternative due to the natural abundance and low cost of sodium. Among them, sodium-ion hybrid capacitors (NICs) are particularly attractive, as they combine the high energy density of batteries with the high power density and long cycle life of supercapacitors, thus representing a promising technology for renewable energy integration.

The main goal of this thesis was the design, synthesis and characterization of new carbon materials to be used as electrode components in NICs. The research focused on overcoming key limitations of current carbon electrodes, namely insufficient reversible capacity, poor rate capability, and low coulombic efficiency. In addition, the work emphasized the employ of sustainable synthesis strategies, including the use of biomass-derived carbon precursors and environmentally benign dopants.

The novelty of this research lies in the combination of two complementary strategies to overcome the main limitation in the development of this technology, that, is, the design of a battery-type negative electrode able to match the fast kinetics of the adsorption-type positive electrode:

1. Nanostructuring of disordered and porous carbons through salt-templating (endo-templating) methods, yielding sponge-like morphologies that minimize Na^+ diffusion resistance.

2. Sulfur-doping using either elemental sulfur or magnesium sulfate ($MgSO_4$), to enhance pseudocapacitive charge storage mechanisms and improve electrochemical performance.

Results

The synthesis of nanostructured carbons via salt-templating produced sponge-like materials characterized by interconnected thin carbon walls, providing short Na^+ diffusional pathways (Figure 1a). As a result, these materials exhibited enhanced rate performance, retaining significant reversible capacity at high current densities (140-179 mAh g^{-1} at 10 A g^{-1}). Systematic optimization revealed that precursor-to-salt ratios above 3:1 were ideal for achieving the desired sponge morphology.

Sulfur-doping experiments demonstrated that the doping temperature plays a decisive role. At 600–650 °C, the incorporation of sulfur enhanced the structural disorder of the carbons (increasing interlayer spacing and defect concentration) and improved their electrochemical behavior. Both elemental sulfur and $MgSO_4$ were evaluated as doping agents. $MgSO_4$ proved particularly attractive due to its dual role as a sulfur source and porogen, generating highly porous structures when combined with inert salts. This strategy led to the development of a versatile synthesis route capable of producing both battery-type (negative electrode) and capacitor-type (positive electrode) carbons (Figure 1b).

The optimized S-doped, sponge-like carbons displayed improved initial coulombic efficiency (ICE >70 compared to 50 for non-doped materials), higher sodium storage capacity (410 and 515 mAh g^{-1} at 0.1 A g^{-1} compared to 150 and 307 mAh g^{-1} for non-doped materials), and excellent stability during prolonged cycling (retention of capacity between 90 and 95% after 200 galvanostatic charge–discharge cycles at 0.2 A g^{-1}). Importantly, sulfur doping not only increases the overall capacity of the carbon materials, but also enhances sodium storage at low potentials (<1.5 V vs. Na^+/Na). This is the capacity effectively exploited in full cell operation, as previously observed in our own work and consistently reported in the literature.

For the positive electrodes, the carbon sponges were further activated, either through conventional activation or by taking advantage of the dual role of $MgSO_4$, which at high temperatures not only serves as a sulfur dopant but also as an effective activating agent. This approach yielded highly porous carbons with surface areas as high as 2600 m^2 g^{-1}, ideally suited for fast ion adsorption/desorption in sodium-ion capacitors.

Full NIC devices were assembled using the optimized negative and positive electrodes following the strategies described above. These devices delivered competitive energy densities combined with high power densities, as illustrated by Ragone-like plots (100-114 Wh kg-1 at low powers and 41-72 Wh kg^{-1} at ~24 kW kg^{-1})(Figure 1a y b). Moreover, long-term cycling tests confirmed the durability of the devices, which showed capacity retentions higher than 97 % after 10000 cycles at 2 A g^{-1}.

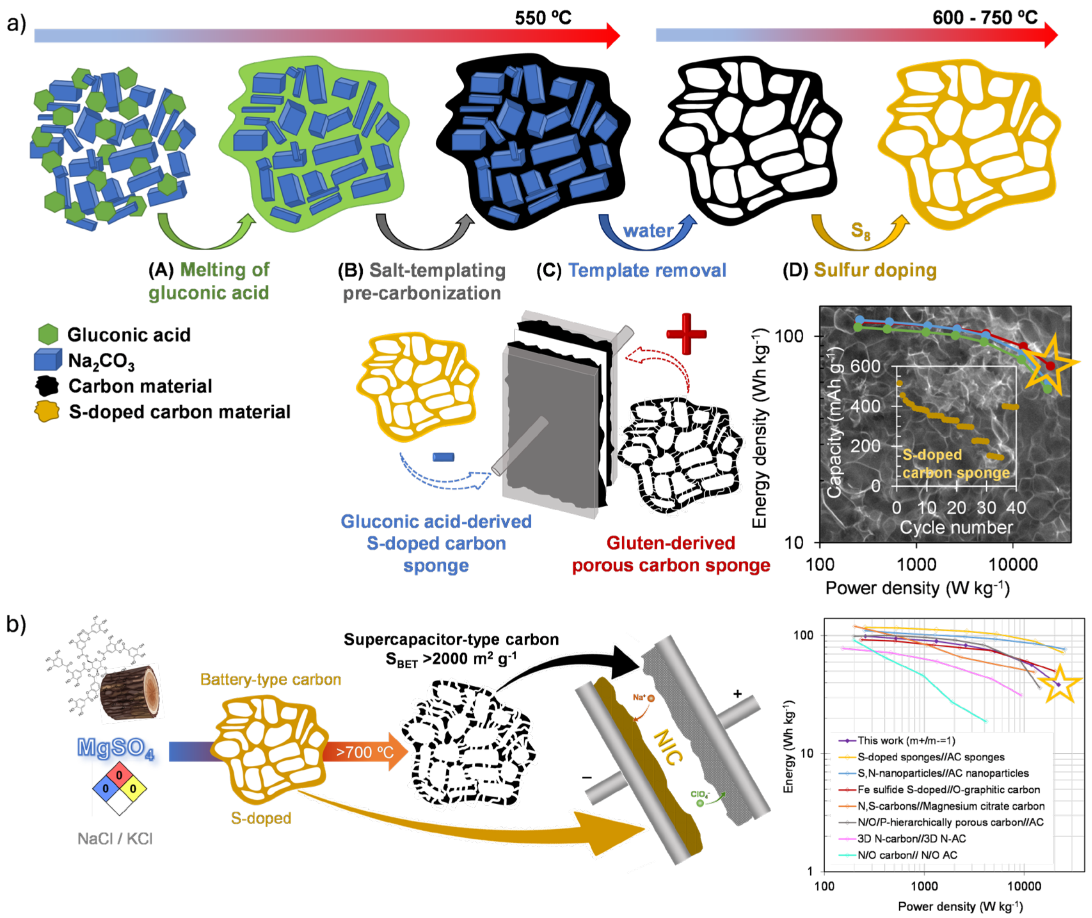

Figure 1. a) Experimental strategy used for the synthesis of the S-doped carbon sponges and Ragone-like plot showing the energy/power performance of the NICs. b) Synthesis scheme followed for the preparation of foam-like and highly porous, foam-like carbons from tannic acid using magnesium sulfate and Ragone-like plot showing the energy/power performance of the NICs compared to the state-of-the-art.

Conclusions

This thesis demonstrates that nanostructuring and sulfur-doping are effective strategies for tailoring the properties of carbon materials towards their application as negative electrodes in sodium-ion capacitors. Nanostructured, sponge-like carbons shortened the diffusional pathways, improving thereby the high-rate performance. Sulfur-doping enhanced the pseudocapacitive contributions and improved the initial coulombic efficiency. $MgSO_4$ has been proven to be an effective dual-function reagent, acting as both sulfur source and porogen depending on the synthesis temperature, constituting a versatile method for production of negative and positive electrode carbons. The developed NIC devices exhibited an optimized trade-off energy and power densities together with remarkable cycle life.

Overall, this doctoral research contributes to the sustainable development of sodium-based energy-grade materials and provides useful guidelines for the design of next-generation hybrid capacitors.

Related publications

[1] S. Payá, M. Sevilla, N. Díez. Biomass-derived carbon sponges for use as sodium-ion capacitor electrodes. Sustainable Energy & Fuels, 2023; 7 (10), 2378-2389.

[2] S. Payá, M. Sevilla, N. Díez. $MgSO_4$ as an effective, low-temperature sulfur dopant for carbon materials enabling fast sodium storage. ACS Applied Energy Materials, 2024; 7 (21), 10061-10072.

[3] S. Payá, M. Sevilla, N. Díez. A single route for the production of battery-type and capacitor-type electrode materials. Carbon, 2025; 235, 120056.

[4] MD. Casal, N. Díez, S. Payá, M. Sevilla. Cork-derived carbon sheets for high-performance Na-ion capacitors. ACS Applied Energy Materials, 2023; 6 (15), 8120-8131.

Full Thesis can be downloaded from:
https://digibuo.uniovi.es/dspace/handle/10651/79887

Nanostructured biopolymers, bionanofabrication and the path towards a sustainable nanotechnology

Víctor Calvo Peña *(vcalvo@icb.csic.es)*

Presented in 2025, Grupo de Nanoestructuras de Carbono y Nanotecnología (GCNN), Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, 50018, Zaragoza, Spain.

Supervisors: Ana M. Benito Moraleja (ICB-CSIC) and José M. González Domínguez (ICB-CSIC).

Objectives and novelty

This doctoral thesis addresses the need for greener practices in nanotechnology by focusing on nanostructured biopolymers (NBs), a class of biopolymers characterized by at least one dimension in the nanoscale. This nanoscale size imparts enhanced and often novel properties to these nanomaterials compared to their bulk counterparts, such as high surface area, tunable surface chemistry, biodegradability, and mechanical robustness, making them attractive for sustainable applications. The main objective was to develop and investigate sustainable and reproducible approaches to synthesize NBs through both top-down and bottom-up routes, to characterize thoroughly, and to exploit their function as emulsifiers and aqueous dispersants for unidimensional carbon nanomaterials (1D CNMs), such as single-walled and multi-walled carbon nanotubes (SWCNTs, MWCNTs), and carbon nanofibers (CNFs), enabling practical devices.

The novelty of this work lies in: i) the development of reproducible top-down protocols for cellulose nanocrystals (CNCs), chitin nanocrystals (ChNCs), and silk fibroin nanofibers (SFNFs), including the optimization of CNC allomorph control via one-pot H_2SO_4 hydrolysis; ii) development of a rapid, non-destructive method based on dynamic light scattering (DLS) for CNC allomorph identification; iii) Application of NBs to stabilize oil-in-water Pickering emulsions and to disperse 1D CNMs in aqueous media without the use of surfactants or organic solvents, enabling the fabrication of conductive films, thermoelectric textiles, and electrochemical sensors; iv) bionanofabrication strategies through the bottom-up synthesis of bacterial nanocellulose (BNC), exploring alternative media, *in situ* nanomaterial additives, and emulsion templating to tailor porosity and introduce new functionalities.

Results

The one-pot H_2SO_4 hydrolysis was optimized to produce CNCs in both allomorphs (type I and type II), enabling control over the allomorph outcome while maximizing yield and reproducibility. The acid–cellulose contact time emerged as the key parameter governing the crystalline form. Additionally, dynamic light scattering (DLS) was validated as a rapid, non-destructive screening method to identify the allomorph outcome. Protocols were also established for ChNCs via HCl hydrolysis and for SFNFs via a water–$CaCl_2$–ethanol ternary solvent. X-ray diffraction, thermogravimetry, and transmission electron microscopy analyses confirmed high crystallinity and stability of the NBs produced by top-down routes (CNCs, ChNCs, and SFNFs).

As a proof of concept, oil-in-water Pickering emulsions were formulated and systematically compared across different oil/water ratios using each NB and compared for the first time using static light scattering and the visual determination of the emulsion stability over time. The analysis linked emulsion stability, droplet morphology, and interfacial behavior to NB structure. Type I CNCs stabilized emulsions best at 30/70 oil/water ratio, while SFNFs performed better at higher oil content. These results position NBs as sustainable emulsifiers capable of replacing conventional surfactants in selected regimes.

Aqueous dispersions of 1D CNMs (SWCNTs, MWCNTs and CNFs) were prepared and optimized using the prepared NBs. The objective was to achieve stable colloidal systems with high CNM concentrations, avoiding the use of organic solvents or dispersants. Among the NBs tested, type II CNCs consistently outperformed type I CNCs and ChNCs, displaying higher affinity and stabilization efficiency across all CNMs. ChNCs enabled stable dispersions with higher CNM content than type I CNCs. In contrast, SFNFs exhibited a distinct behavior: they were particularly effective in dispersing pristine CNTs but showed limited performance with CNFs.

The CNM/NB dispersions were extensively characterized to assess colloidal stability, structure, and surface chemistry. Selected formulations were used as water-based inks to fabricate conductive films via drop-casting and spray-coating. Electrical and electrochemical characterizations revealed competitive performance, especially for type II CNC-based films, which exhibited lower surface resistance and enhanced electrochemical response. Additionally, post-deposition thermal treatment improved the conductivity by 1 to 5 orders of magnitude, particularly in films with initially higher resistance. These results validate the use of NBs as green and effective dispersants for CNMs in water, enabling the scalable fabrication of conductive films without the need for hazardous chemicals.

Furthermore, the inks were tested in two proof-of-concept applications: thermoelectric textiles and electrochemical sensors. Prototype e-textiles were fabricated by dip-coating cotton fabrics with CNF/type II CNC inks and evaluated in terms of electrical conductivity, thermoelectric performance, and laundering resistance, confirming their feasibility for flexible and sustainable energy harvesting. Modified electrodes enabled the detection of two emerging contaminants in water, demonstrating the potential of these inks for environmental monitoring using greener fabrication methodologies.

Lastly, BNC was investigated as a bottom-up NB produced by bacterial synthesis, with strategies developed to tailor its structure and functionality through culture media optimization, incorporation of in situ nanomaterial additives (SWCNTs, carbon dots, and ChNCs), and oil-in-water emulsion templating. This approach enabled the fabrication of porous BNC composites with tunable porosity, controlled by emulsion composition and droplet size. These results consolidate bionanofabrication as a promising strategy for sustainable nanomaterial production, exploiting the inherent capabilities of living systems to conduct nanoscale synthesis.

Conclusions

This thesis demonstrates significant progress in sustainable nanotechnology through the development of reproducible and optimized synthesis protocols for nanostructured biopolymers (CNCs, ChNCs, SFNFs and BNC) and their validation in different applications. Using water as the sole processing medium, the work enables the dispersion of 1D-CNMs without organic solvents and surfactants, preserving their intrinsic properties and allowing the fabrication of functional inks for conductive films, thermoelectric textiles, and electrochemical sensors. The results highlight the excellent ability of NBs as aqueous dispersants, to stabilize Pickering emulsions under selected conditions, and the versatility of bionanofabrication strategies to tailor BNC composites.

These findings help balance sustainability with functionality, while opening new avenues for practical implementation of these green nanomaterials in energy and environmental technologies. Nevertheless, challenges remain, including scalability, reproducibility, and performance optimization at industrially relevant throughputs. Future work should refine NB synthesis and processing windows, broaden application domains and device integration, and incorporate sustainability assessments to quantify environmental benefits. Overall, this work consolidates nanostructured biopolymers as key enablers of green nanotechnology, emphasizing the importance of interdisciplinary collaboration to drive advancements in this field and highlighting the potential of NBs for applications in energy, sensing, and environmental remediation.

Acknowledgements

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Related publications

[1] Álvarez-Sánchez M.A., Calvo V., Carrera C., Colom E., Güemes L., Martínez-Barón C., González-Domínguez J.M. Emerging carbon nanotechnology. Advances and Thoughts from a Young Perspective. Bol. del Grupo Español del Carbón. 2021, 60, 8-19.

[2] Calvo V., González-Domínguez J.M., Benito A.M., Maser W.K. Synthesis and Processing of Nanomaterials Mediated by Living Organisms. Angewandte Chemie International Edition. 2022, 61, e202113286.

[3] Calvo V., Álvarez-Sánchez M.A., Güemes L., Martínez-Barón C., Baúlde S., Criado A., González-Domínguez J.M., Maser W.K, Benito A.M. Preparation of Cellulose Nanocrystals: Controlling the Crystalline Type by One-Pot Acid Hydrolysis. ACS Macro Letters. 2023, 12, 152-158.

[4] Calvo V., Fuentes L., Berdejo D., González-Domínguez J.M., Maser W.K., Benito A.M. Oil-in-Water Pickering Emulsions Stabilized with Nanostructured Biopolymers: A Venue for Templating Bacterial Cellulose. International Journal of Molecular Sciences. 2023, 24-17, 13141.

[5] Fuentes L., Calvo V., Berdejo D., González-Domínguez J.M., Maser W.K., Benito A.M. Bionanofabricación como Principio Sostenible de Obtención de Nanocelulosa Bacteriana. Boletín del Grupo Español del Carbón. 2023, 68, 11-14.

[6] Vázquez-Conejo B., Martínez-Barón C., Calvo V., García-Bordeje E., Ansón-Casaos A., González-Domínguez J.M., Maser W.K., Benito A.M. Nanoestructuras de Carbono Unidimensionales: Procesado Sostenible en Agua a Través de Nanocristales de Celulosa. Boletín del Grupo Español del Carbón. 2023, 68, 6-10.

[7] Calvo V., Paleo A.J., González-Domínguez J.M., Muñoz E., Krause B, Pötschke P., Maser W.K., Benito A.M. The Aqueous Processing of Carbon Nanofibers Via Cellulose Nanocrystals as a Green Path Towards e-Textiles with N-Type Thermoelectric Behaviour. Carbon. 2024, 217, 118640.

[8] Calvo V., Martínez-Barón C., Vázquez-Conejo B., Dominguez-Alfaro A., Paleo A.J., Villacampa B., Ansón-Casaos A., Maser W.K., Benito A.M., González-Domínguez J.M. Carbon Nanomaterials-Based Inks and Electrodes Using Chitin Nanocrystals. ACS Sustainable Chemistry Engineering. 2024, 12, 15980–15990.

[9] Calvo V., Martínez-Barón C., Fuentes L., Maser W.K., Benito A.M., González-Domínguez J.M. Nanocellulose: The Ultimate Green Aqueous Dispersant for Nanomaterials. Polymers. 2024, 16, 1664.

[10] Martínez-Barón C., Calvo V., Hernández-Ferrer J., Villacampa B., Ansón-Casaos A., González-Domínguez J.M., Maser W.K., Benito A.M. Towards Sustainable TiO2 Photoelectrodes Based on Cellulose Nanocrystals as a Processing Adjuvant. RSC Sustainability. 2024, 2, 2015–2025.

[11] Martínez-Barón C., Calvo V., Álvarez-Sánchez M.A., Maser W.K., Benito A.M., Ansón-Casaos A., González-Domínguez J.M. Carbon Nanotube Film Electrodes Enabled by Nanostructured Biopolymers through Aqueous Processing. Physical Chemistry Chemical Physics. 2025, 27, 16756-16767.

[12] Baquero-Aznar V., Calvo V., González-Domínguez J.M., Maser W.K., Benito A.M., Salvador M.L., González-Buesa J. Novel Egg White Protein–Chitin Nanocrystal Biocomposite Films with Enhanced Functional Properties. Polymers. 2025, 17(18), 2538.

[13] Calvo V., Venegas C.J., Sierra-Rosales P., Miralles-Cuevas S., Cabrera A., Maser W.K., Benito A.M., González-Domínguez J.M. Real-Time Electrochemical Sensing of a Wastewater Contaminant Using Green Nanomaterials: From Lab Optimization to Pilot-Scale Validation. Submitted. 2025.

[14] Güemes L., Calvo V. et al. Bottom-up Assembly of Cellulose Nanocrystals as a Green entry to Structured Functional Carbons. Submitted. 2025.

Full Thesis can be downloaded from:
https://zaguan.unizar.es/record/162673

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

María González-Ingelmo

maria.ingelmo@incar.csic.es

Presented in July 2025, Facultad de Química de la Universidad de Oviedo.

Supervisors: Patricia Álvarez Rodríguez and Victoria García Rocha (INCAR-CSIC).

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.

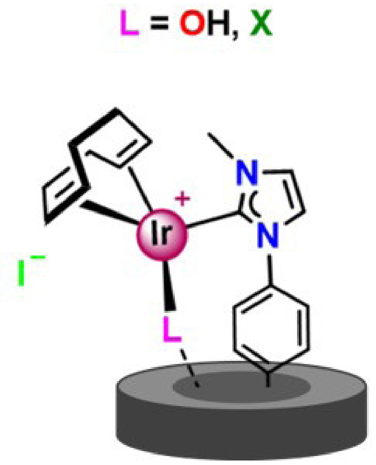

Figure 1. Structure of Ir-NHC complex supported on reduced graphene oxide.

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.

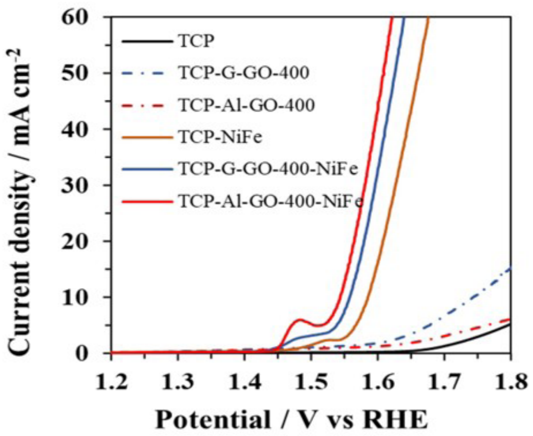

Figure 2. Linear sweep voltammograms of the different electrodes prepared in this work, recorded at 10 mV s^{-1} in the potential range of 1.2-1.8 V vs RHE in KOH 1 M.

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

[1] González-Ingelmo, M., Álvarez, P., Granda, M., Rocha, V.G., González, Z., Sierra, U., Sánchez-Page, B., Jiménez, M.V., Pérez Torrente, J.J., Blasco, J., Subías, G. On the study of the preparation of graphene-anchored NHC-iridium catalysts from a coke-like waste with application in water splitting. Applied Surface Science 655 (2024) 159556.

[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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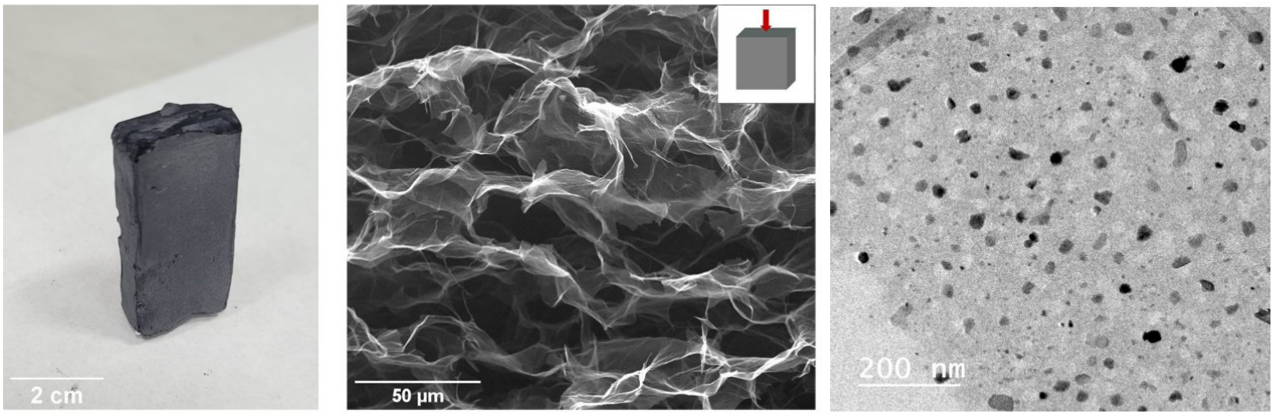

Figure 3. Macroscopic aspect, SEM and TEM images of Ni-doped graphene aerogels (from left to right)

Synthesis of two-dimensional materials through electrochemical exfolation for energy storage

Daniel Fernández Carrasco

daniel.fernandez@incar.csic.es

Presented iin 2025, Departamento de Química de Materiales, Instituto de ciencia y Tecnología del Carbono (INCAR-CSIC).

Supervisors: Juan Ignacio Paredes Nachón and Fabian Suárez García (INCAR-CSIC).

Objectives and novelty

The rapid growth in the demand for renewable energy has underscored the importance of developing energy storage devices with high energy density, stability, and low cost, which are essential for meeting future energy and environmental demands. Conventional materials such as activated carbons, metal oxides or conducting polymers face intrinsic limitations in terms of energy density, cycling stability, or cost-effectiveness. In this context, two-dimensional (2D) materials, such as graphene and transition metal dichalcogenides (TMDs), have sparked strong interest owing to their high surface area, tunable electronic structure and chemical versatility.

However, the widespread implementation of these materials is still hindered by the lack of scalable and environmentally friendly synthesis methods. Classical approaches for producing graphene and TMDs, such as chemical oxidation–reduction, mechanical exfoliation or chemical vapor deposition, either involve hazardous reagents, require sophisticated infrastructure or are not suitable for large-scale production. Similarly, liquid-phase exfoliation strategies typically rely on ultrasonication in organic solvents, which raises concerns regarding reproducibility, cost and sustainability.

This work aims to obtain 2D materials, particularly graphene and TMDs, via electrochemical exfoliation for use in electrochemical energy storage devices (supercapacitors, hybrid aqueous zinc-ion capacitors and lithium storage). Specifically, anodic exfoliation has enabled the rapid and straightforward production of oxidized graphene with good structural quality and extensive aromatic domains, making it an ideal precursor for porous graphene with uniformly distributed nanometric pores. This is reflected in its good electrochemical performance as a supercapacitor electrode. Anodic exfoliation also allows control over the population and type of oxygen functional groups in the resulting graphenes through appropriate choice of electrolyte, enhancing properties such as wettability and charge storage capacity for hybrid zinc-ion storage devices. In addition, cathodic exfoliation in aqueous electrolyte has facilitated access to metallic TMD nanostructures (NbSe2, NbS2, and VSe2) with morphological control (nanorolls and nanosheets), which directly affects the behavior of these materials as electrodes for lithium storage.

Results

In the realm of graphene, one of the main contributions of this thesis was the investigation of a novel strategy based on anodic exfoliation of graphite to obtain highly oxidized graphene, which represents a very attractive alternative due to its simplicity and speed in comparison to conventional methods for obtaining highly oxidized graphene (such as graphene oxide prepared by the Hummers method). At the same time, and different to the case of such conventional methods, the anodic route affords oxidized graphene of a relatively good structural quality, characterized by dense and small oxidized domains, where the oxygen functional groups are concentrated, interspersed with relatively extensive aromatic domains. This makes the present anodic oxidized graphene an ideal precursor for the generation of holey graphene, where the hole (pores) generated through selective attack of the oxidized domains present small and uniform dimensions (a few nanometers), and also exhibit a uniform spatial distribution across the nanosheet.

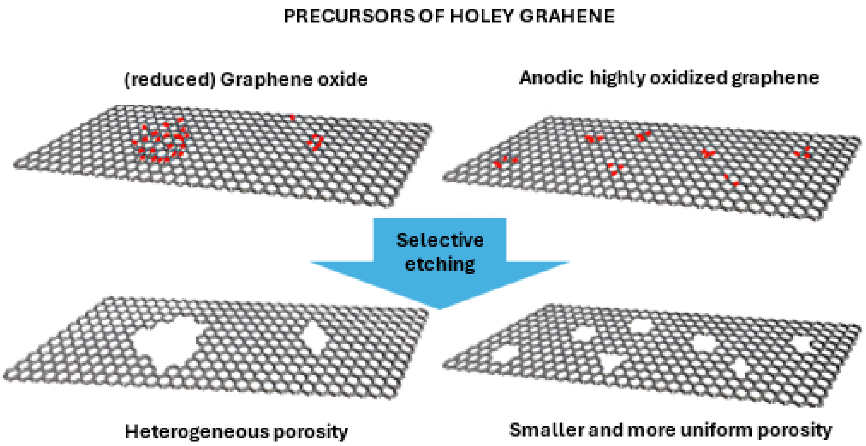

Figure 1. Schematic representation of the preparation of holey graphene from structurally and chemically different precursors.

These structural features translate into graphenes with improved electrochemical performance when used as active materials in supercapacitors, showing higher charge storage capacity and energy density compared to similar materials derived from standard, Hummers-based graphene oxide.

The anodic exfoliation route to graphene has not only allowed modulating the oxidation degree of the resulting nanosheets, but it has also enabled some control over the populations of oxygen functional groups present in these graphenes. Specifically, it has been shown that the type and relative amount of these groups can be tuned through appropriate choice of the aqueous electrolyte used for anodic exfoliation. In particular, this ability has afforded graphenes with increased amounts of carboxyl groups, which in turn was shown to improve such properties as the wettability, and led to higher charge storage capacities when these graphenes were used as cathode material in aqueous zinc-ion hybrid capacitors. Further to this, the performance of electrodes based on this type of graphene has been enhanced by incorporating redox-active molecules, such as flavin mononucleotide, and coating zinc electrodes with carboxyl-enriched graphene has been proven to improve their cyclability and stability by preventing dendrite formation, a factor that limits the applicability of batteries and capacitors using metallic zinc as the anode.

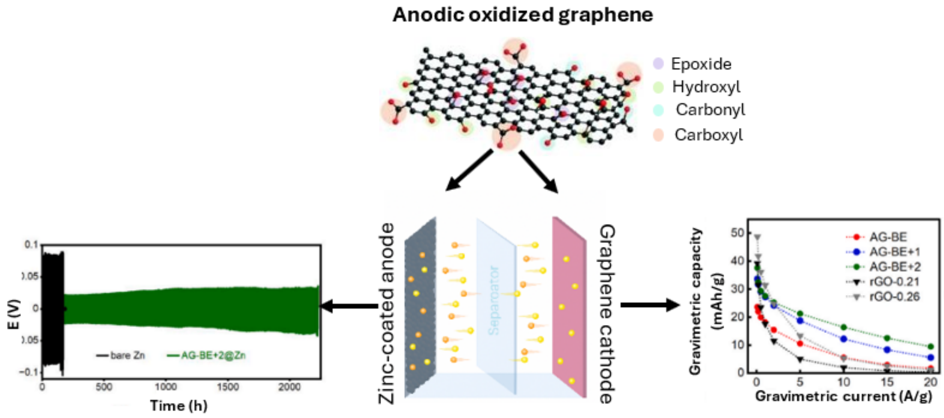

Figure 2. Schematic representation of the diverse applications of modular graphene obtained through anodic electrochemical exfoliation.

Finally, cathodic exfoliation in an aqueous medium has been investigated as an efficient method for obtaining 2D nanosheets of metallic TMDs, mainly $NbSe_2$, but also NbS_2 and VSe_2, also with control over the material's final morphology (e.g., nanoroll vs. nanosheet). Such morphological control has led to TMD-based electrodes with different behaviors in electrochemical lithium storage. Specifically, electrodes based on $NbSe_2$ nanorolls exhibit a higher storage capacity than that of nanosheets, attributable to the less compact packing of the electrode with the former, which facilitates a better electrolyte access. Moreover, it was shown that the mechanism of cathodic exfoliation developed here for these TMDs is entirely different from that occurring in common electrochemical (cathodic or anodic) exfoliation processes of layered materials.

Conclusions

This thesis has demonstrated the potential of electrochemical exfoliation as a versatile, scalable, and environmentally friendly strategy for the synthesis of relevant two-dimensional materials, i.e., graphene and metallic TMDs, tailored for energy storage applications.

For graphene, anodic exfoliation enables the production of highly oxidized materials with preserved structural quality, combining oxidized domains and extended aromatic regions. This makes them ideal precursors for holey graphene with nanometer-sized pores, leading to enhanced supercapacitor performance. The anodic route also allows control over oxygenated functional groups through electrolyte selection, with carboxyl enrichment improving wettability and charge storage in zinc-ion hybrid capacitors. Performance is further boosted by redox-active molecules and by coating zinc anodes with carboxyl-rich graphene, which suppresses dendrites and enhances stability.

In parallel, cathodic exfoliation in aqueous media provides metallic TMDs with tunable morphologies that strongly affect lithium storage behavior. The results also reveal a distinct exfoliation mechanism for metallic TMDs compared to other layered materials.

References

[1] Carrasco D. F., Álvarez-Rubiera E., Villar-Rodil S., Martínez-Jódar A., Tascón J. M. D., Suárez-García F., Paredes J. I., *Chemically tuning graphene via anodic exfoliation for enhanced performance in aqueous zinc-based electrochemical energy storage* applications, Carbon, 228 (2024) 119293.

[2] Carrasco D. F., García-Dalí S., Villar-Rodil S., Munuera J. M., Raymundo-Piñero E., Paredes J. I., NbSe2 nanosheets/nanorolls obtained via fast and direct aqueous electrochemical exfoliation for high-capacity lithium storage, ACS Appl. Energy Mater., 6 (13) (2023) 7180–7193.

[3] Carrasco D. F., Paredes J. I., Villar-Rodil S., Suárez-García F., Martínez-Alonso A., Tascón J. M. D., An electrochemical route to holey graphene nanosheets for charge storage applications, Carbon, 195 (2022) 57–68.

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