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

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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

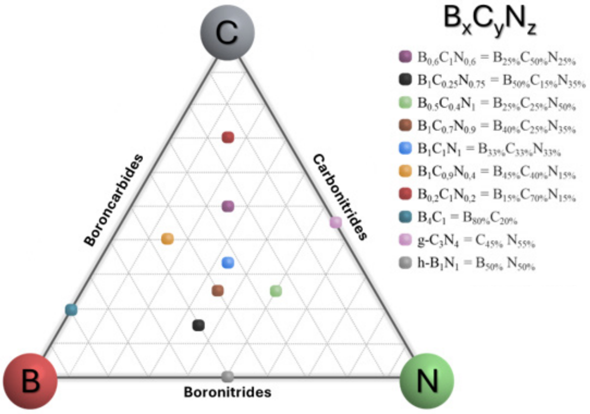

Figure 1. Ternary phase diagram of the BxCyNz materials [9]
Figura 1. Diagrama de fase ternario de los materiales BxCyNz

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.

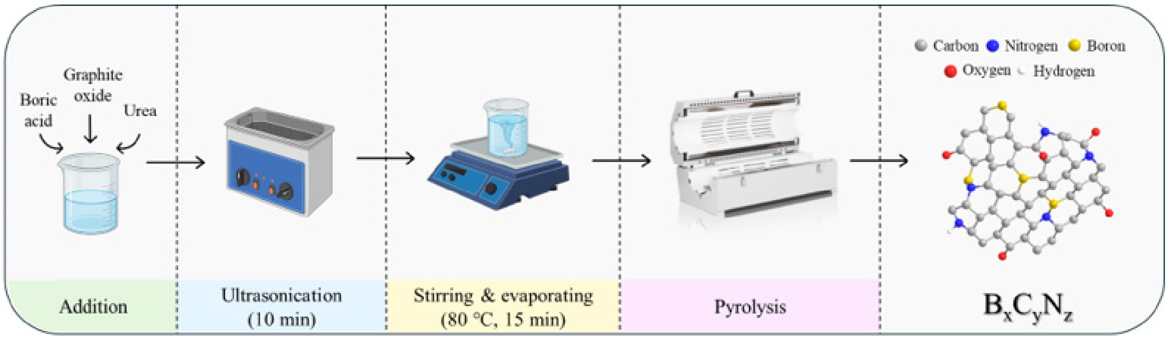

Figure 2. Scheme of BCN synthesis
Figura 2. Esquema de la síntesis de **BCN**

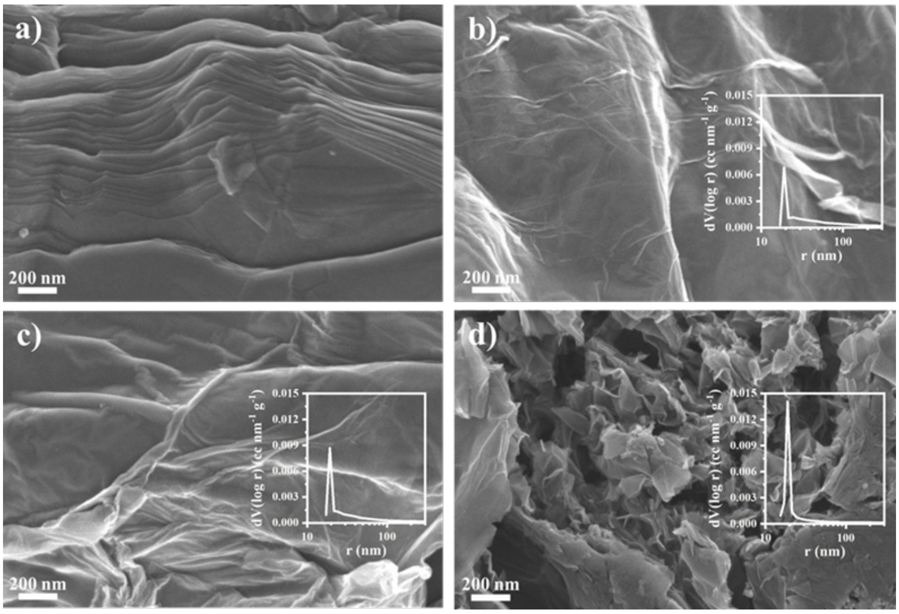

Figure 3. SEM images of a) GrO and b) 700-10h-BCN, c) 800-10h-BCN and d) 900-10h-BCN, including its pore size distribution.
Figura 3. Imágenes SEM de a) GrO y b)700-10h-BCN, c) 800-10h-BCN y d) 900-10h-BCN, incluyendo sus distribuciones de tamaño de poro.

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].

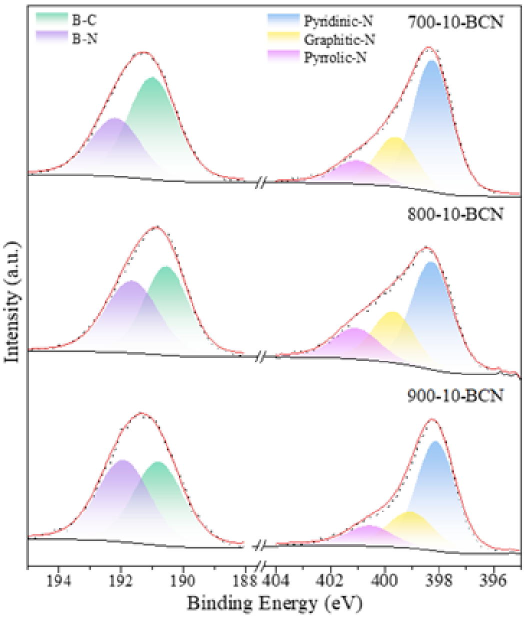

Figure 4. High-resolution core level B1s and N1s XPS spectra of BCN calcined at different temperatures.
Figura 4. Espectros XPS de alta resolución de B1s y N1s de BCN calcinado a diferentes temperaturas.

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.

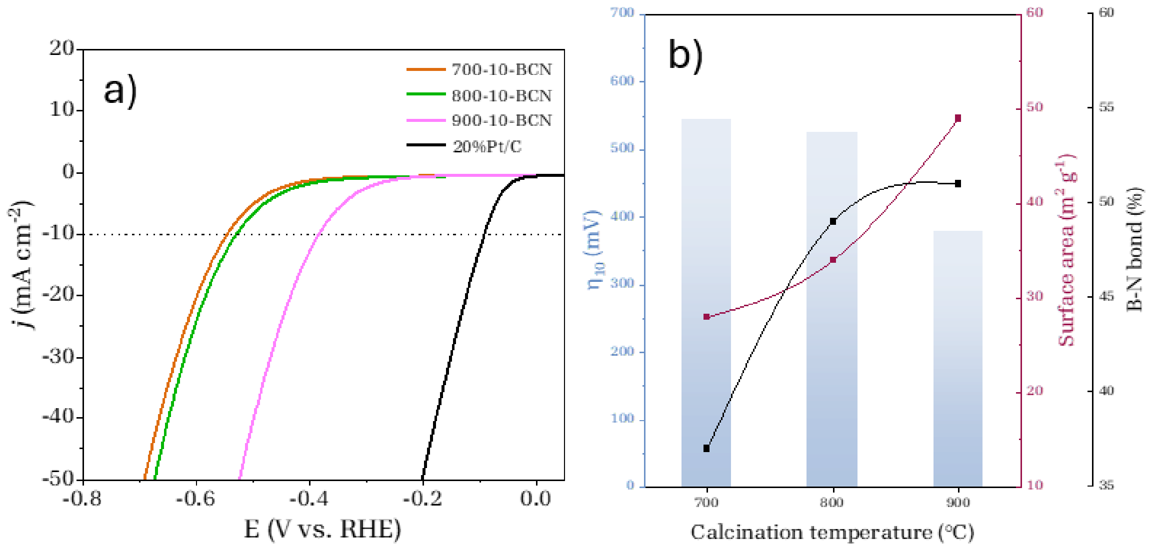

Figure 5. a) Linear Sweep Voltammetry, b) the corresponding Tafel plots, and c) η_{10} and surface area vs. calcination temperature of BCNs calcined at different temperatures.

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		η_{10} (mV)
			L_A (nm)	L_C (nm)	
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		η_{10} (mV)
			L_A (nm)	L_C (nm)	
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.

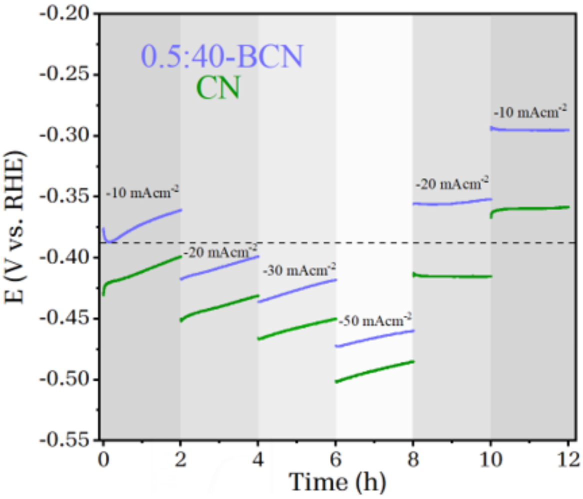

Figure 6. CP curves recorded at different current densities of CN and 0.5:40-BCN.

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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