

Defects, Doping, and Curvature: Structure–Property–Function Design of Carbon Nano-Onions for Metal-Free ORR Electrocatalysis

Marcin Zajac, Anthony Papathanassiou, Kinga Ciecuch-Tymoniuk, Krzysztof Brzezinski, and Marta E. Plonska-Brzezinska*



Cite This: <https://doi.org/10.1021/acsanm.5c05570>



Read Online

ACCESS |



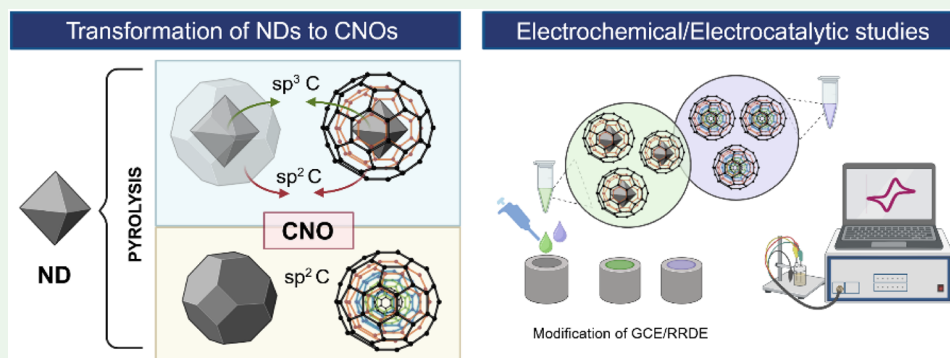
Metrics & More



Article Recommendations



Supporting Information



ABSTRACT: The interplay between defects, heteroatom doping, and surface curvature in carbon nanostructures governs their electronic transport and catalytic properties, yet it remains poorly understood. Here, we elucidate how structural defects, N/O functionalities, and high curvature collectively modulate morphology, conductivity, and oxygen reduction reaction (ORR) activity in carbon nano-onions (CNOs) derived from nanodiamonds (NDs). Ultradispersed NDs with tailored surface terminations are thermally transformed at 1,150 and 1,650 °C to generate partially graphitized core–shell nanostructures and fully converted, highly graphitized CNOs, respectively. X-ray photoelectron spectroscopy and electrochemical analysis reveal that pyridinic- and graphitic-N and carbonyl/phenolic O at curvature-induced defect sites define the defect chemistry, enabling fine control over charge transport and interfacial reactivity. Rotating ring-disk electrode studies show that optimally graphitized, defect-accessible CNOs (1,650 °C) deliver high specific capacitances, near-diffusion-limited ORR currents, with the number of electrons transferred per O₂ molecule during ORR approximately 4.0, and a ≤10% H₂O₂ selectivity in alkaline media. Within a curvature-engineering framework, concentric graphenic layers introduce a Gaussian curvature that concentrates local fields and tunes *OOH binding, while continuous sp² networks minimize resistive losses. This work establishes a structure–property–function concept for “curved” nanocarbons and defines design rules for next-generation, metal-free CNO electrocatalysts.

KEYWORDS: carbon nano-onion, defect, doping, conductivity, electrocatalysis, oxygen reduction reaction

1. INTRODUCTION

A new generation of electrocatalysts has been developed, in which the defective surface of materials promotes multiple proton-coupled electron transfer and mass transportation.¹ Defects are widely present in nanomaterials and are recognized as the active sites for electrocatalytic processes, which tune electronic and surface properties in the local region.^{1,2} The defects may be created via *in situ* synthesis or by the application of postmodification methods during the preparation process of nanomaterials. The theory linking defect structures to the electrocatalytic properties of nanocatalysts is the most common.^{3,4} At the center of our interest is the oxygen reduction reaction (ORR), a heterogeneous gas–liquid–solid process central to many electrochemical energy conversion and storage devices. The ORR proceeds either via a direct four-electron

(4e[−]) pathway to H₂O or a two-step two-electron (2e[−]) route through H₂O₂, depending on the catalyst and electrolyte.

Carbon nanostructures (CNs) demonstrate excellent ORR activity with high stability and CO and methanol tolerance.⁵ Among them, graphene- and graphdiyne-based materials are compelling electrocatalysts owing to their high electrical conductivity and mechanical robustness, large specific surface areas with microporosity, facile defect formation (e.g., pentagon,

Received: December 8, 2025

Revised: February 23, 2026

Accepted: March 3, 2026

edge, and vacancy defects), and high charge-carrier mobility.^{5,6} Such defects modify the electronic structure and surface properties, increase the density of accessible active sites, and optimize chemisorption of key intermediates, thereby accelerating ORR kinetics.^{7,8} For example, He et al. correlated higher sp^3/sp^2 ratios in reduced graphene oxide with increased defect content and improved activity, consistent with a larger population of active sites.⁷ Intrinsic carbon defects have been shown to promote electron transfer in metal-free ORR catalysts.⁵ Defect identity also matters. Pentagon defects redistribute electron density and can enhance ORR reactivity, whereas a pristine hexagonal lattice does not provide the same degree of activation.^{9,10} Beyond creating active sites, the topology of defective carbon networks improves interactions with reactants and facilitates mass transport across porous frameworks.¹¹

Heteroatom doping further amplifies these effects.¹² Dopants with electronegativity distinct from carbon (N and O) redistribute charge within the lattice, strengthen the binding of oxygenated intermediates, and improve electron transfer during ORR.^{13,14} Nitrogen-doped carbons, for instance, lower the barrier for O_2 activation and perform well even in acidic media.¹⁵ The presence of nitrogen in the carbon structure introduces localized states in the electronic structure, increasing the density of states near the Fermi level, thereby facilitating electron transfer during the ORR.¹⁶ Introducing vacancy defects, including oxygen-containing vacancies, can also increase the surface area and tailor electronic properties, yielding higher ORR rates over a broad range of operating conditions.¹⁷

The second parameter that should be particularly taken into account is “surface curvature”, defined in terms of radius of curvature, Gaussian curvature, and mean curvature,¹⁸ which describes the nanoscale bending of catalyst surfaces (e.g., sharp tips, concave depressions, convex protrusions) and acts as a critical structural parameter that couples morphology to electronic structure, local strain, and reaction microenvironment.¹⁹ In contrast to planar surfaces, curved surfaces generate compressive/tensile microstrain, redistribute electric fields and ion concentrations, and modulate the adsorption energies of key intermediates, thereby governing reactant activation, diffusion, and overall reaction kinetics.^{19,20} Carbon-based materials provide prototypical platforms for such “curvature engineering” in electrocatalysis. High-curvature carbon architectures (onion-like carbons and carbon spheres) offer tunable electronic structures, high conductivity, and stability.²⁰

Multilayered fullerenes (carbon nano-onions, CNOs) are graphitic CNs composed predominantly of hexagonal rings, interspersed with pentagons, heptagons, and occasional four- and eight-membered rings that serve as surface defects.²¹ Dislocations, atomic vacancies, and stacking faults contribute to the electrochemically active surface area intrinsic to graphitic carbons.²² Both experimental and theoretical studies show that annealing conditions during synthesis or post-treatment significantly affect the CNO structure and physicochemical properties, and that defects predominate in their electrochemical behavior in aqueous electrolytes.^{23,24} Defects and heteroatom dopants synergistically enhance the electrocatalytic properties of the CNOs. Structural imperfections generated during synthesis or via intentional doping (e.g., N or S) create localized active sites that facilitate charge transfer and strengthen reactant interactions.^{23–25} Our previous studies show that N-doped CNOs display markedly improved catalytic activity toward H_2O_2 due to an optimized charge distribution associated

with the presence of N and faster electron-transfer kinetics resulting from the high microporosity of CNOs.²³ The inherently high surface area of undoped CNOs (up to $\sim 454\text{ m}^2\text{ g}^{-1}$) and of N-doped CNOs (up to $\sim 383\text{ m}^2\text{ g}^{-1}$),²³ and their concentric, onion-like architecture further enhance mass transport and reactant accessibility. N-doping modifies the local electronic structure, increasing the density of states near the Fermi level and stabilizing oxygenated intermediates, thereby improving durability. Surface functional groups associated with dopants can also contribute pseudocapacitance alongside double-layer capacitance.²³ Synthesis using annealing protocols offers practical levers to tune defect density and distribution, enabling CNOs with balanced structural integrity and active-site abundance.^{24,25} Additionally, CNOs, consisting of concentric, graphenic carbon layers, exemplify this concept: their densely packed nanopores and highly curved sp^2 surface enhance mass transfer, graphitization, and stability.^{26,27} Furthermore, curvature-induced electric fields and charge redistribution have been shown to boost electrocatalytic activity and improve electrocatalytic selectivity.²⁷

Motivated by this framework, we prepared a series of CNOs from ND precursors using a modified Kuznetsov method, which involved annealing under an inert atmosphere at 1,150 or 1,650 °C and reduced pressure.²⁸ Three ND substrates with distinct surface functionalities (unfunctionalized, amine-functionalized, and oxygen-functionalized) yielded six CNO samples spanning different defect densities and heteroatom contents. These materials were comprehensively characterized and evaluated electrochemically for ORR to establish structure–property–function relationships among intrinsic defects, heteroatom doping, and electrocatalytic performance in carbon nanostructures with high curvature.

2. EXPERIMENTAL SECTION

2.1. Materials

All chemicals and solvents used were commercially available and used without further purification: sodium chloride ($\sim 98\%$, Sigma-Aldrich), lithium perchlorate ($LiClO_4$, 98%, Sigma-Aldrich), sodium perchlorate ($NaClO_4$, 98%, Sigma-Aldrich), tetraethylammonium chloride hydrate ($(Et_4)NCl$, 98+%, Sigma-Aldrich), anhydrous ethanol ($EtOH$, 99.8%, POCH Gliwice), mesoporous carbon (Sigma-Aldrich; surface area $>48.8\text{ m}^2\text{ g}^{-1}$; pore size $>0.13\text{ cm}^3\text{ g}^{-1}$), and graphitic carbon nitride (Carbodeon; particle size $>30\text{ }\mu\text{m}$; surface area $>35\text{ m}^2\text{ g}^{-1}$). All aqueous solutions for electrochemical studies were prepared using deionized water, which was further purified with a Milli-Q system (Millipore). Commercially available nano-diamond (ND) powder with a crystal size between 4 and 6 nm (Carbodeon μ Diamond Molto; Carbodeon μ Diamond Amine; Carbodeon μ Diamond Vox; and ND content greater than 97 wt %) was used for the preparation of the CNOs. The modified Kuznetsov method for preparing CNOs involved applying a thermal treatment under an inert atmosphere and reduced pressure to ultradispersed ND particles for 1 h at either 1,150 °C or 1,650 °C.²⁸ The Kuznetsov method ensures high process efficiency, with approximately 90% of CNs assumed to be obtained from ND nanoparticles. It is a highly efficient process in materials chemistry. After the ND-to-CNOs transformation, only the amorphous carbon adsorbed on the CNOs surface was removed. The obtained CNOs (after the transformation during the pyrolysis of NDs to CNOs) were then annealed for 1 h at 400 °C to remove amorphous carbon from the CN's surface. Next,

the CNOs were dried in a furnace at 120 °C overnight before use.

2.2. Methods

High-resolution transmission electron microscopy (HRTEM) was performed by using a Titan G2 HRTEM microscope (FEI Company) equipped with a field emission gun (FEG). The electron beam accelerating voltage was 300 kV. HRTEM imaging of the sample microstructure was performed in bright-field mode using a CCD camera as the detector. Before analysis, the samples were ground in an agate mortar to form a fine powder. Into the obtained powder, 99.8% EtOH (POCH, Poland) was poured to form a dispersion, which was placed in an ultrasonic homogenizer for 10 s. The resulting slurry was taken with a pipette and placed on Cu grids (200 mesh/inch) coated with carbon-stabilized Formvar (Ted Pella, USA) until the solvent evaporated.

For powder X-ray diffraction (XRD), the samples were loaded into glass capillaries (Hampton Research, Glass Number 50) with a diameter of 1.0 mm. The XRD data were measured using CuK α radiation at 293 K on an XtalLAB Synergy diffractometer (Rigaku) equipped with the Hybrid Pixel two-dimensional detector HyPix-6000HE. For all experiments, the sample-to-detector distance was set to 148 mm, and the data were recorded over a 2θ angle range from 10° to 100° using the standard ϕ scan procedure. In all experiments, the exposure time was 300 s. The XRD data were processed by using *CrystAlisPro* software (Rigaku).

X-ray photoelectron spectroscopy (XPS) was performed using an ultrahigh vacuum chamber (PREVAC) with a base pressure below 10^{-8} mbar using an Al K α nonmonochromatic radiation source (1486.7 eV; 12 kV; 12 mA; VG Scienta SAX 100) and a monochromator (VG Scienta XM 780). Detection of emitted photoelectrons was carried out using a Scienta R4000 hemispherical analyzer. A low-resolution survey run (0–1200 eV) at a pass energy of 200 eV was conducted. The C 1s, O 1s, and N 1s high-resolution spectra were recorded at a pass energy of 50 eV at RT. All the spectra were fitted by Shirley background subtraction before applying Gaussian–Lorentzian functions using CasaXPS software (Casa Software Ltd.).

Broadband Dielectric Spectroscopy (BDS) was conducted by employing a Solartron 1260 Frequency Response Analyzer (FRA), equipped with a Broadband Dielectric Converter (BDC, Novocontrol) for carrying out high-precision measurements of complex impedance. The operating frequency varied from 1 Hz to 1 MHz. The entire calibration and measuring procedure was monitored through WinDeta (Novocontrol) software. The sample holder comprises two parallel bronze plates, part of a standard Alpha Active Cell (Novocontrol), connected to the FRA by suitable coaxial wiring. Free-standing pellets were prepared by compressing powder by using a uniaxial press. The diameter of the disc-shaped samples was 5 mm, and the thickness was 1–1.5 mm. The parallel surfaces of the disc-shaped specimens were covered with conductive silver paste. Complex impedance measurements were performed under ambient conditions and RT.

A PGSTAT 302N potentiostat (Metrohm Autolab B.V., Utrecht, The Netherlands), equipped with a three-electrode cell, was used for cyclic voltammetry (CV). The working electrode was a glassy carbon electrode (GCE; 2 mm diameter, Bioanalytical Systems, Inc.). Before each experiment, the GCE was polished with extrafine SiC paper (Buehler), then with 0.3 μ m alumina and 0.25 μ m diamond suspensions (MetaDi II,

Buehler), and rinsed thoroughly with deionized water and EtOH. The counter electrode was a Pt flag (0.5 cm²). The reference electrode was Ag/AgCl (Ag wire immersed in 0.1 M AgCl) housed behind a ceramic frit (Bioanalytical Systems, Inc.). Prior to measurements, the GCE surface was modified by drop-casting an ethanolic dispersion of the synthesized material (2 mg mL⁻¹, 0.012 mg—amount of material applied to the surface of the GC electrode) containing a small amount of carbon paint (CP; SPI Supplies, USA). The solvent was allowed to evaporate at room temperature. Dispersions (CNOs or NDs in EtOH) were ultrasonicated for 30 min to ensure a uniform suspension. In all electrochemical analyses, an aqueous solution with the different 0.1 M supporting electrolytes (NaCl, NaClO₄, LiClO₄, and (Et₄)NCl) was used. Oxygen was removed from the solution by purging with Ar of technical purity.

The electrocatalytic activity of CNOs and NDs toward the ORR was evaluated by linear sweep voltammetry (LSV) using a rotating ring-disk electrode (RRDE). Measurements were carried out in O₂-saturated 0.1 M KOH (Chempur, Poland) and 0.1 M H₂SO₄ (Stanlab, Poland) at a scan rate of 10 mV s⁻¹, with an Autolab PGSTAT302N potentiostat (Metrohm Autolab, Utrecht, The Netherlands). A standard three-electrode configuration was employed: a GC disk with a surrounding platinum ring (Pt/GC) as the working electrode, an Ag/AgCl (saturated KCl) reference electrode, and a Pt wire counter electrode.

Catalyst inks were prepared by dispersing 2 mg of CNOs or NDs in 1 mL of EtOH, followed by the addition of carbon paint (SPI Supplies, West Chester, USA). The suspensions were ultrasonicated for 30 min to ensure uniform dispersion of CNOs or NDs in EtOH, and 20 μ L was drop-cast onto the RRDE surface and dried under ambient conditions.

Before measurements, the electrolyte was saturated with high-purity O₂ and a continuous O₂ flow was maintained during LSV scans. RRDE data were analyzed to determine the electron transfer number and the selectivity of the HO₂⁻ intermediate. LSV curves were recorded over a potential range from 0.0 to -0.8 V vs Ag/AgCl at RRDE rotation speeds of 250–2500 rpm, in 250 rpm increments. For benchmarking, the ORR performance of commercial 10 wt % Pt/C (Sigma-Aldrich, St. Louis, MO, USA) was measured under identical conditions.

3. RESULTS AND DISCUSSION

3.1. Structural Properties of ND-Derived CNOs Using HRTEM, XRD, and XPS Studies

Ultradispersed ND powders with three surface chemistries (Molto, Amine, and Vox; Table 1) were thermally treated in a low-pressure He atmosphere at 1,150 or 1,650 °C to form CNOs (Figure 1). The precursor functionality was retained as heteroatom dopants in the products, with nitrogen for Amine-derived CNOs (CNO Amine) and oxygen for Vox-derived

Table 1. Conditions for Obtaining CNOs Using Pyrolysis and Product Designations

Starting materials	Pyrolysis (°C)	Assignment of products
ND Molto	1,150	CNO Molto 1150
	1,650	CNO Molto 1650
ND Vox	1,150	CNO Vox 1150
	1,650	CNO Vox 1650
ND Amine	1,150	CNO Amine 1150
	1,650	CNO Amine 1650

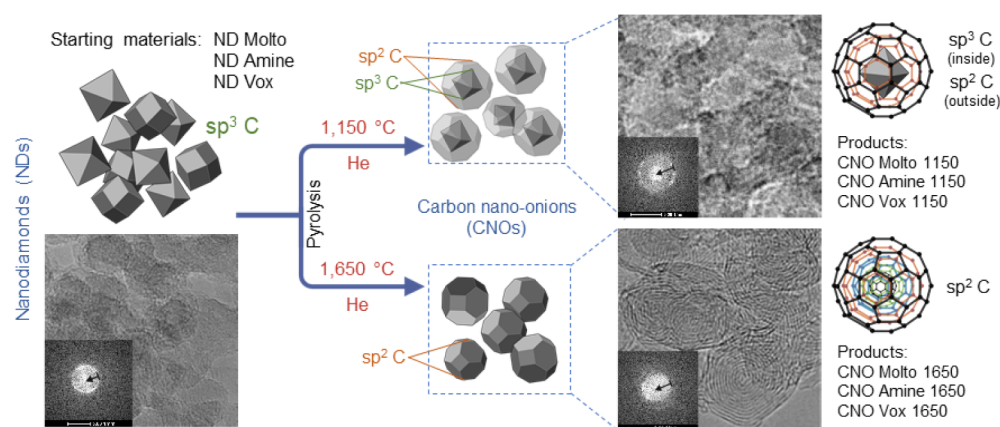


Figure 1. Schematic representation of the transformation of NDs to CNOs at the temperatures of 1,150 °C and 1,650 °C during pyrolysis (He atmosphere).

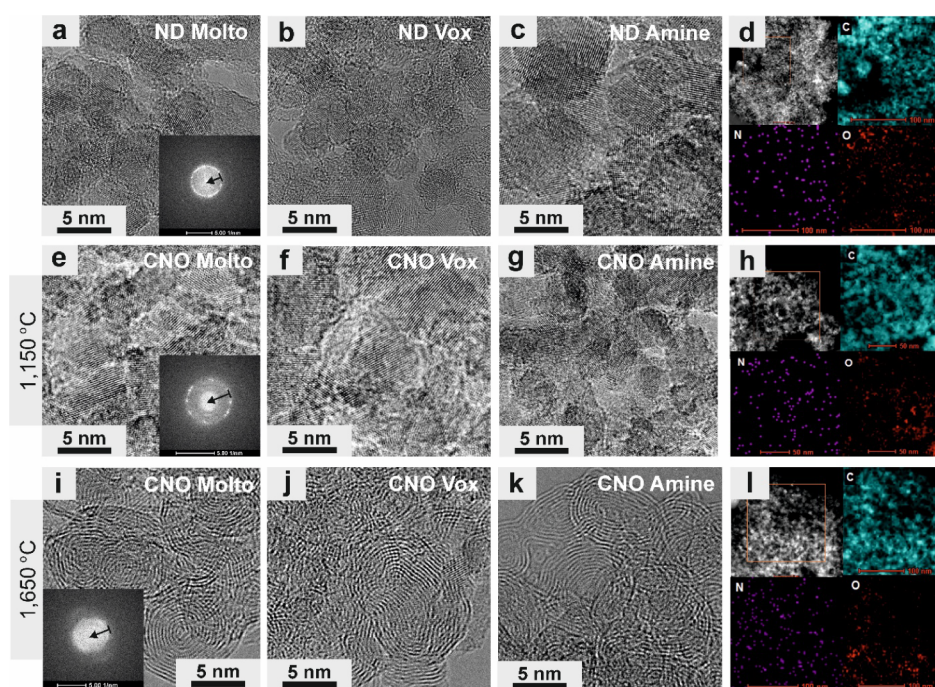


Figure 2. Representative HRTEM images of NDs: (a) Molto, (b) Vox, and (c) Amine; of CNOs (e, i) Molto, (f, j) Vox, and (g, k) Amine, obtained at temperatures of (e, f, g) 1,150 °C and (i, j, k) 1,650 °C. STEM-EDX analysis of (d) NDs and (h, l) CNOs Amine.

CNOs (CNO Vox). The annealing controlled the extent of the NDs-to-CNOs transformation, defect density, and surface chemistry. HRTEM of the starting NDs shows faceted crystallites with primary sizes of ~ 5 – 6 nm (Figure 2a–c). Particles form loose to moderately compact aggregates (tens to a few hundred nanometers). No substantive differences are observed among the Molto, Vox, and Amine NDs at this stage. Selected-area electron diffraction (SAED) displays broadened rings at diamond positions on a diffuse amorphous background (inset, Figure 2a), and lattice fringes with a dominant spacing of ~ 0.206 nm, consistent with (111) planes of cubic diamond.²⁹ Under annealing at 1,150 °C, NDs begin to graphitize: diamond cores contract while concentric sp^2 layers nucleate (Figures 1, 2e–g and S1). HRTEM reveals that the product consists mainly of core–shell hybrids with two to three graphenic layers encapsulating a residual diamond core. Particles remain relatively uniform in size but are often polyhedral rather than spherical, and shell discontinuities and defects are

common—features consistent with the defect-rich, heteroatom-doped CNOs obtained under these conditions. Increasing the annealing temperature to 1,650 °C further tunes the shell order, as reflected in defect content (Figures 1, 2i–k and S2).

Thermal treatment of ND Molto at 1,650 °C yields complete conversion to spherical, multishelled CNOs (CNO Molto 1650, Figure 1). HRTEM images show quasi-spherical particles with a mean diameter of 5 – 6 nm (Figures 2i–k and S2). SAED displays diffuse rings indexed to graphitic carbon [(002), (100)/(101)] (Figure 2i, inset), with pronounced broadening indicative of finite graphitic domains and turbostratic stacking. At 1,150 °C, a minority of particles retain a core–shell character, whereas at 1,650 °C, closed layers are well developed (Figure 1), more uniform, and the amorphous fraction is largely suppressed. In N-doped CNOs, the onion-like architecture is preserved: concentric, well-closed graphenic layers with near-spherical morphology and only occasional surface irregularities (Figures 2, S1, and S2). Continuous lattice fringes are intermittently

perturbed by bending, dislocations, and edge terminations, consistent with a moderate defect density rather than amorphization.

STEM-EDX maps confirm the presence of N and O in materials annealed at both temperatures (Figure 2d, h, and l); heteroatom signals colocalize with the carbon framework, and no dopant-rich clusters or secondary phases are detected within the method's sensitivity. Thus, N incorporation proceeds without compromising shell integrity, yielding structurally robust, electrically continuous particles with a uniform distribution of heteroatom sites and a controlled population of defects—features expected to enhance O₂ adsorption and stabilize ORR intermediates.

Oxygen-derived CNOs obtained from ND Vox are highly heterogeneous (Figures 2f and j, S1 and S2). Layers are discontinuous, graphitic ribbon segments and amorphous regions are common, and hollow cores, sharp terminations, and occasional openings are observed. Annealing at 1,650 °C drives the system toward full graphitization; concentric, closed layers predominate, and edge-terminated ribbon motifs persist within curved layers (Figure 2j). The observed microstructures are consistent with oxygen-assisted reconstruction and localized etching at the diamond core/shell interface: outward diffusion of oxygen can “unzip” nascent layers, interacting with sp³ and sp² carbon to generate needle- or ribbon-like fragments.^{30,31} Differential etching exposes sp² carbon at diamond grain boundaries and promotes localized graphitization at these sites. The coexistence of closed layers and ribbon motifs suggests that oxygenated precursors bias step-flow reorganization along low-curvature domains, producing locally planar fragments that relieve strain and create a high density of edge sites. Consequently, oxygen not only redirects the growth pathway but also imprints chemically reactive motifs onto the carbon framework.²⁵

X-ray diffraction (XRD) of the CNs (Figure 3) resolves three structural contributions: diamond-like sp³-hybridized carbon, hexagonal graphitic sp²-hybridized carbon, and a disordered/turbostratic component with sp²/sp³ bonding. For NDs, sharp reflections at $2\theta = 43.5^\circ$ (111), 75.8° (220), and 92.0° (311) are observed, with (111) being the most intense, confirming a well-crystallized diamond cubic phase.^{32,33} A weak, broad feature near $2\theta \approx 22^\circ$, assigned to graphitic (002), indicates a minor sp² carbon atom contribution consistent with sp²-terminated ND surfaces. Upon conversion to CNOs, graphitic signatures dominate: a broad (002) band centered at $2\theta = 25.3^\circ$ and an in-plane (100) peak at $2\theta = 43.4^\circ$, both characteristic of hexagonal graphite (Figure 3).^{34,35}

The most prominent evolution is the growth and pronounced broadening of the (002) peak, indicating a transition from predominantly sp³ bonding to sp²-rich layers. The width and slight shift of (002) reflect small coherent stacking domains, turbostratic disorder, curvature-induced strain, and defects expected for concentric onion-like layers. Notably, the graphitic (100) peak at 43.4° overlaps with the diamond (111) peak at 43.5° ; however, the attenuation of the higher-order diamond reflections (220, 311), together with the emergence of graphitic bands, confirms progressive graphitization of NDs. Across all CNOs, the overall patterns are similar (Figure 3). Still, the XRD pattern analysis reveals the coexistence of graphitic and diamond-like domains. Each material exhibits a dominant, asymmetric out-of-plane (002) reflection at $2\theta \approx 25.3^\circ$ with a low-angle shoulder near 22° , indicative of a distribution of interlayer spacings and stacking faults in turbostratic sp²-

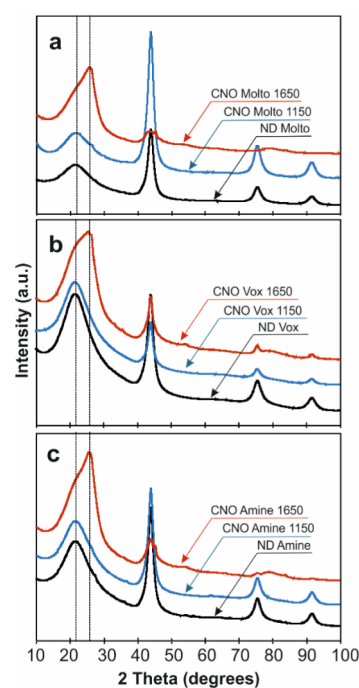


Figure 3. XRD patterns of ND and CNO series: (a) Molto, (b) Vox, and (c) Amine. Black lines represent ND samples, blue lines represent CNOs obtained at 1,150 °C, and red lines represent CNOs obtained at 1,650 °C.

hybridized carbon atoms, along with carbon atoms of intermediate sp²/sp³ character.

Among the series, CNO Vox 1650 shows the greatest (002) broadening (Figure 3b), consistent with the highest level of structural disorder within its graphitic layers (smaller stacking domains and increased microstrain/defect density). The width and asymmetry of the (002) peak, maximal for CNO Vox 1650, trace finite crystallite sizes, strain, and defects that were generated during the ND-to-CNO transformation. Overall, the XRD data support a microstructural model in which NDs evolve into CNOs composed of curved graphitic layers (sp²) interspersed with disordered carbon at sp²/sp³ interfaces.³³ This trend is supported by HRTEM (Figure 2), which reveals discontinuous multilayer graphene and deviations from a spherical morphology, features that broaden the (002) profile.

X-ray photoelectron spectroscopy (XPS) confirms the conversion of NDs to CNOs and the incorporation of heteroatoms (Figure 4, Tables S5–S7). C 1s dominates survey spectra with clear N 1s and O 1s signals across materials, indicating successful N/O atom incorporation. Assessment of the percentages of C, N, and O atoms in XPS spectra requires separation of these into components corresponding to different chemical forms, defined by their binding energies (BEs). BEs were charge-corrected to the sp² C=C component at 284.5 eV in C 1s (Table S5).³⁶ Deconvolution of the C 1s region shows a predominantly sp³ C–C/C–H domain for NDs and graphitic sp²-hybridized carbon atoms for onion-like architectures (Figures 4 and 5, Tables S5–S7).

The XPS spectra for NDs indicate a mixed sp³/sp² surface with substantial oxygen functionality. The sp³ C–C/C–H peaks at 285.0 and 285.6 eV confirm a diamond core,^{37,38} while the 284.5 eV sp² C=C component evidences surface graphitization and/or curved graphene-like layers typical of the functionalized NDs (NDs Amine and Vox).³⁶ The minor 283.9 eV signal points

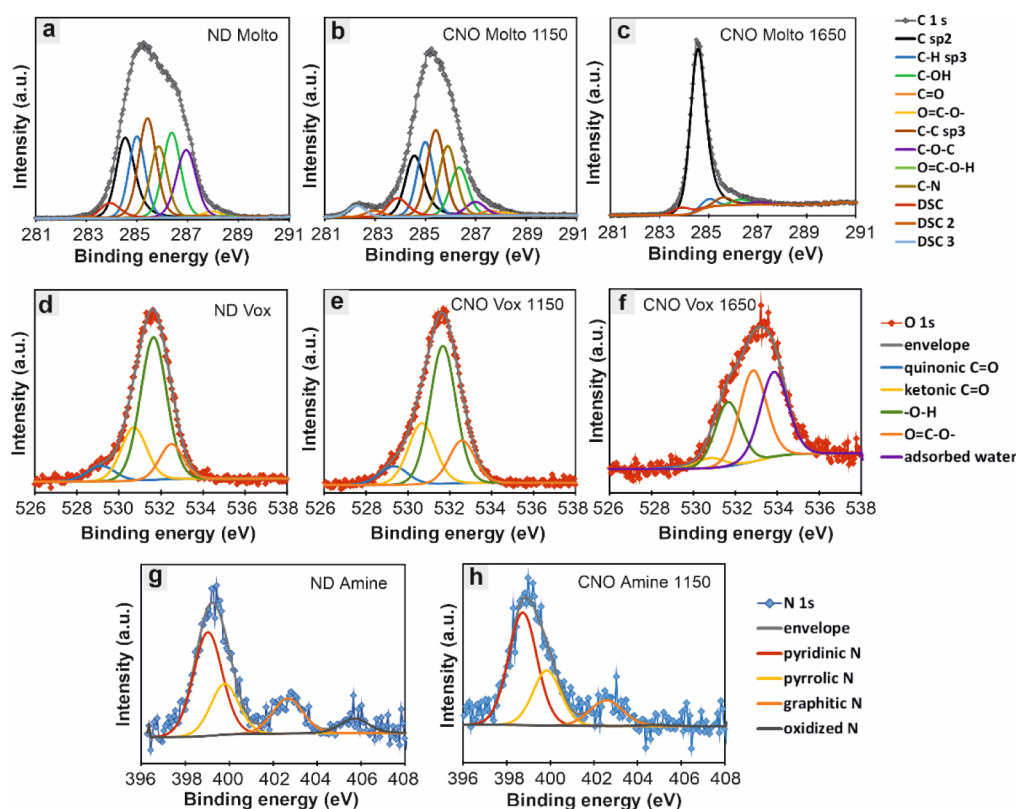


Figure 4. Deconvolution of XPS spectra of the C 1s spectral region of (a) NDs Molto, (b) CNOs Molto 1150, and (c) CNOs Molto 1650; the O 1s spectral region of (d) NDs Vox, (e) CNOs Vox 1150, and (f) CNOs Vox 1650; and the N 1s spectral region of (g) NDs Amine and (h) CNOs Amine 1150.

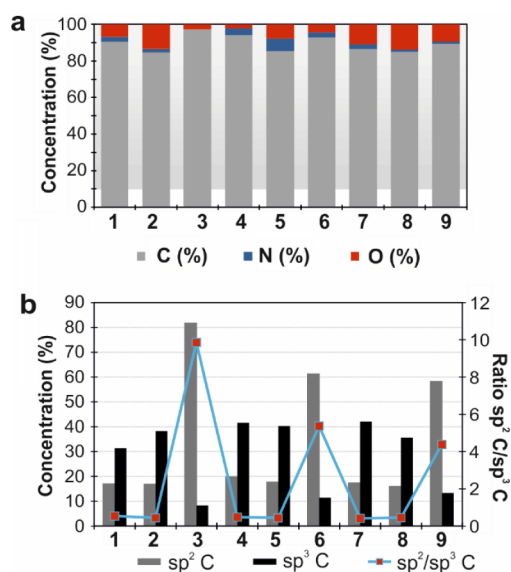


Figure 5. (a, b) Analysis of XPS studies. Assignment of elements determined for NDs and CNOs was obtained from the deconvolution of the XPS C 1s, O 1s, and N 1s spectra. Legends: 1 (ND Molto), 2 (CNO Molto 1150), 3 (CNO Molto 1650), 4 (ND Amine), 5 (CNO Amine 1150), 6 (CNO Amine 1650), 7 (ND Vox), 8 (CNO Vox 1150), and 9 (CNO Vox 1650).

to defect-rich sp^2 at grain boundaries; its presence supports localized reconstruction at the ND surface. This peak indicates a specific type of structural defect, typically associated with defective carbon environments or unsaturated bonding

configurations.³⁹ After the transformation of NDs into CNOs, the C 1s spectra are dominated by the sp^2 C=C component at 284.5 eV for all CNOs, consistent with concentric graphitized layers (Tables S5 and S6). A minor contribution at 285.0 and 285.6 eV arises from sp^3 C–C/C–H, reflecting a curvature-induced rehybridization.

Quantitatively, the sp^2/sp^3 -hybridized C atoms ratio extracted from the 284.5 vs 285.0–285.6 eV components provides a convenient metric of CNs' graphitization and successful NDs' transformation into CNOs (Figure 5). NDs and CNOs formed at 1,150 °C, and the amount of sp^2 C atoms is almost constant, below 20 at. % relative to the concentration of all carbon atoms. The amount of sp^2 C increases significantly, reaching 81.8 at. % (CNO Molto 1650) (Tables S6 and S7 and Figure 5b). For CNO Amine 1650 and CNO Vox 1650, the amount of sp^2 -hybridized C is about 60 at. %. Higher-binding-energy components in the range of ~286.3–288.8 eV also indicate oxygen-containing moieties.^{40–42} Finally, a π – π^* shakeup satellite at ~290.5–291.5 eV confirms the presence of delocalized π systems, supporting the preservation of extensive sp^2 domains within the CNOs.

The N 1s spectra resolve multiple N environments, confirming the incorporation of heteroatoms into NDs and CNOs. Components at ~398.8 eV are assigned to pyridinic-N (substitutional, sp^2),⁴³ whereas features at ~399.7–400.3 eV correspond to pyrrolic/amine-like N in five-membered rings or terminal amines (Figure 4g, h; Tables S5–S7). A peak at 402.9 ± 0.6 eV is attributed to graphitic (quaternary) N substitutional within the sp^2 lattice,⁴⁴ which is expected to enhance electronic conductivity and stabilize the π network, while oxidized N–O

species (N-oxide/NO/NO₂) contribute to the higher binding energy at ~ 405.0 eV (Tables S5–S7).⁴⁴

The N-doped CNOs exhibit the highest overall N levels: CNO Amine 1150 reaches 1.6 at. % N, the same amount as the precursor ND Amine (1.6 at. %) and the higher-temperature product CNO Amine 1650 (below 1 at. %, Table S5). The coexistence of pyridinic and graphitic signatures suggests that the N atoms occupy positions in the CNO layers, providing a balance of pyridinic and graphitic sites that can modulate the interfacial activity and charge transport in electrocatalytic reactions.

XPS O 1s spectra reveal quinonic C=O, ketonic C=O/O=C–O–, ether-like, and carboxyl/phenolic groups that enhance the surface polarity of CNOs (Figure 4d–f). Together, the sp²-rich backbone with mixed N-phenomena and O-containing groups corroborates a conductive, curvature-stabilized CNO architecture bearing chemically active edge sites. The O 1s spectrum of the CNOs resolves into well-defined components consistent with oxygen functionalities, such as carbonyl/quinone (C=O) at 529.2 ± 0.2 eV, ketonic C=O/O=C–O– (~ 530.7 eV), ether-like/epoxy (C–O–C) at ~ 530.7 – 531.7 eV, and phenolic/carboxylate/ester (Ph–OH, O=C–O–) at 532.6 ± 0.2 eV, with a broad, weak high-energy shoulder above ~ 533.8 eV attributable to adsorbed H₂O/oxygen (Tables S5–S7). Structurally, quinone and phenolic groups populate the outer layers' defect sites, increasing hydrophilicity and supporting proton/OH[–] interactions. XPS O 1s quantification shows that CNO Vox derived from ND Vox contains the highest overall O levels among the materials studied (Figures 4g–i and 5a; Table S5). The ND Vox precursor exhibits 8.4 at. % O, whereas CNO Vox 1150 reaches 10.6 at. % O. Increasing the transformation temperature to 1,650 °C lowers the O content to 7.3 at. %. A similar trend is observed for the other CNOs (Molto and Amine); annealing at 1,150 °C yields 10 at. % O, while processing at 1,650 °C reduces the O level to 2–4.8 at. %. Expressed on a mass basis, the corresponding O contents are approximately 2% points higher. These data indicate that the 1,150 °C ND-to-CNO conversion promotes the formation or retention of O-containing surface groups (likely associated with defect-rich layers). In contrast, subsequent high-temperature treatment (1,650 °C) drives deoxygenation and increased graphitization, diminishing the concentration of oxygen functionalities.

3.2. Broadband Dielectric Spectroscopy

Broadband Dielectric Spectroscopy (BDS) over a wide frequency range can identify direct current (dc) conductivity and polarization (capacitance) effects arising from inherent (bulk) electric charge trapping in a disordered material. Individual conductivity and polarization mechanisms can be distinguished from any undesirable electrode polarization. BDS is an experimental tool for examining whether an electrode material facilitates electric charge transport toward internal, large-capacitance surface areas (as indicated by the direct current conductivity and dielectric constant) for electrochemical reactions. The real part of the complex electrical conductivity $\sigma'(f)$ as a function of frequency f is depicted in Figure 6a. The conductivity spectra are as follows: $\sigma'(f) = \sigma_{dc} + Af^n$, where σ_{dc} denotes the dc conductivity, A is a fitting parameter, and n is a fractional exponent. σ_{dc} actually corresponds to the frequency-independent value of $\sigma'(f)$.

In Figure 6b, $\log \sigma_{dc}$ is depicted for ND precursors and CNO derivatives. We observe that the dc conductivity of different NDs

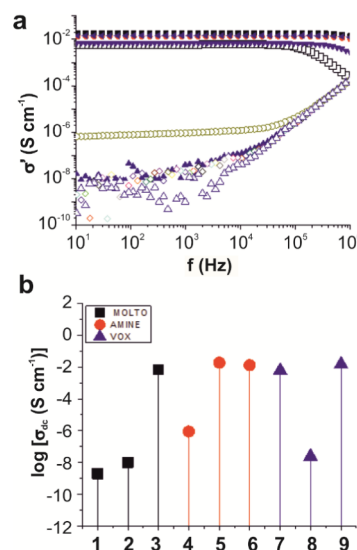


Figure 6. (a) The real part of the electrical conductivity σ' as a function of frequency measured at room temperature for: ND Molto (open triangles), CNO Molto 1150 (open rhombus), CNO Molto 1650 (inverted full triangle), ND Amine (open circles), CNO Amine 1150 (full squares), CNO Amine 1650 (full polygon), ND Vox (open squares), CNO Vox 1150 (full triangles), and CNO Vox 1650 (inclined full triangle). (b) Logarithm of the dc conductivity $\log \sigma_{dc}$ of NDs and derived CNOs. Legends: 1 (ND Molto), 2 (CNO Molto 1150), 3 (CNO Molto 1650), 4 (ND Amine), 5 (CNO Amine 1150), 6 (CNO Amine 1650), 7 (ND Vox), 8 (CNO Vox 1150), and 9 (CNO Vox 1650).

varies significantly depending on surface chemistry: functionalized ND Amine and ND Molto exhibit dc conductivities about six and two orders of magnitude higher, i.e., $\log \sigma_{dc} = -6.06(6)$ S cm⁻¹ and $-2.2256(6)$ S cm⁻¹, respectively, compared with that of unfunctionalized ND Molto ($\log \sigma_{dc} = -8.7(5)$ S cm⁻¹).

To understand why σ_{dc} changes in different NDs, it is necessary to recall a fundamental equation: $\sigma_{dc} = \sum_i N_i q_i \mu_i$, where the index i counts the number of individual conduction mechanisms, each contributing with a density N_i of charge carriers q_i of mobility μ_i . N_i is proportional to the abundance of (intrinsic or extrinsic) defects. μ_i is a measure of the interaction of the transferring i -charge with its environment (and, thus, is sensitive to the degree of disorder, heterogeneity, and microstructural landscape). HRTEM results (Section 3.1) indicate that the microstructural characteristics do not change significantly across different NDs; therefore, the differences in their properties σ_{dc} are attributed to the varying charge-carrier densities of surface N or O defects. The macroscopic dc conductivity of NDs may also be affected by an amorphous carbon layer covering some ND aggregates (Section 3.1, Figures 2, S1, and S2).

The dc conductivity of both unfunctionalized NDs and functionalized ones converges toward a value of $\log \sigma_{dc} \approx -2$ S cm⁻¹ after annealing at 1,650 °C due to the complete conversion of NDs to CNOs. More specifically, for CNO Molto, $\log \sigma_{dc} = -2.1708$ S cm⁻¹. For CNO Amine, the N atoms in the carbon structure introduce localized states in the electronic structure (subsequently increasing the density of states near the Fermi level), facilitating the dc conduction: $\log \sigma_{dc} = -1.8845$ S cm⁻¹. For CNO Vox, the dc conductivity is slightly higher: $\log \sigma_{dc} = -1.8394$ S cm⁻¹, as a result of different competing features, such as the O heteroatom colocalization within the carbon matrix vs

heterogeneity and structural imperfections (we speculate that if a well-shaped CNO Vox of minor conformational disorder could be prepared, the value of the electrical conductivity might be higher than the observed one).

Increasing the pyrolysis temperature of ND Molto results in a systematic increase in dc conductivity, which is offset by the decrease in the ND transformation to spherical CNOs. CNO Amine achieves a saturation conductivity at 1,150 and 1,650 °C, as both temperatures promote the formation of N-doped CNOs consisting of integrated, well-closed, near-spherical graphenic layers with occasional surface irregularities. The substantial heterogeneity observed in HRTEM (Section 3.1), comprising various configuration defects, may account for the low electrical conductivity of CNO Vox 1150, thereby making a detailed correlation of conductivity with a specific type of structural disorder quite challenging. Indeed, as mentioned in Section 3.1, the XRD patterns indicate that among the series, CNO Vox 1650 exhibits the highest level of structural disorder in its graphenic layers, in agreement with the HRTEM results for discontinuous multilayer graphene and deviations from a spherical morphology.

The real part of the (relative) dielectric permittivity $\epsilon'(f)$ captures polarization effects. A frequency-independent regime at low frequencies, which determines the static (relative) dielectric constant ϵ_s , is followed by a gradual drop at high frequencies, extrapolating to the high-frequency value ϵ_∞ . From the $\epsilon'(f)$ spectra depicted in Figure 7a, the dielectric constants of NDs and derived CNOs were estimated (Figure 7b). We note that ϵ_s is proportional to the overall capacity and is a metric of the effective surface area accessible for charge accumulation (and subsequent electrochemical reactions).

The transition of ND Molto to CNO Molto 1150 and CNO Molto 1650 yields a monotonous dielectric constant increase, as

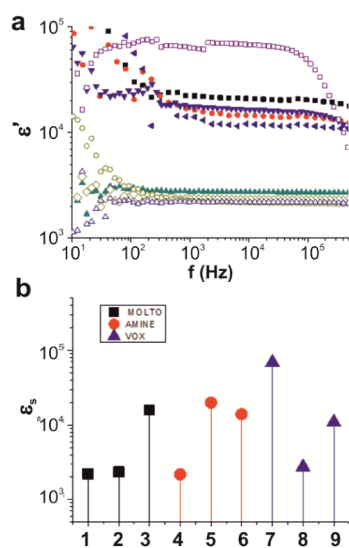


Figure 7. (a) The (relative) static dielectric constant ϵ_s of NDs and derived CNOs: ND Molto (open triangles), CNO Molto 1150 (open rhombs), CNO Molto 1650 (inverted full triangle), ND Amine (open circles), CNO Amine 1150 (full squares), CNO Amine 1650 (full polygon), ND Vox (open squares), CNO Vox 1150 (full triangles), and CNO Vox 1650 (inclined full triangle). (b) The real part of the complex permittivity ϵ' as a function of frequency f , measured at room temperature. 1 (ND Molto), 2 (CNO Molto 1150), 3 (CNO Molto 1650), 4 (ND Amine), 5 (CNO Amine 1150), 6 (CNO Amine 1650), 7 (ND Vox), 8 (CNO Vox 1150), and 9 (CNO Vox 1650).

the produced multilayered CNOs serve as multilayered concentric spherical capacitors. The complete transformation of NDs to CNOs, Molto, and Amine at 1,650 °C improves ϵ_s by about an order of magnitude compared to the values of ND precursors. As mentioned in the preceding paragraph, CNO Vox exhibits the most disorder and heterogeneity among the derived CNOs. Structural defects partially alter the functionality of CNOs as ideal multilayered capacitors. At the same time, imperfections may also partially act as pinning centers for charge trapping; it is unclear how the competition among different charge-trapping mechanisms in ND Vox and its CNO Vox derivatives yields an effective ϵ_s value.

In conclusion, CNOs derived after annealing at 1,650 °C exhibit high electrical conductivities: CNO Molto and Amine 1650 achieve improved conductivities compared to the corresponding NDs, while CNO Vox 1650 retains the high conductivity value of ND Vox. They can, therefore, promote fast electric transport and storage. On the other hand, the values of the static dielectric constant are also optimized in the same manner as the dc conductivity, due to the increased multilayered effective area available for charge storage and microstructural trapping.

Improved electrical conductivities and dielectric constants suggest that large surface areas are readily accessible to charge carriers, facilitating further electrochemical reactions. Coupling sufficient conductivity and capacitance constitutes an intrinsic property of the derived CNOs. Still, the efficiency and functionality of CNO electrodes merge the electrodes' properties with the electrolyte's features. The conversion of Molto and Amine NDs to CNOs during annealing induces (to some extent) systematic changes in σ_{dc} and ϵ_s ; hence, their properties are likely more predictable when, for example, an intermediate temperature (1,150 °C) is applied. On the contrary, the high inhomogeneity and rich variety of structural/configurational defects (which may also annihilate, generate, or intertransform upon annealing) of CNO Vox prevent us from having a general framework on how different annealing processes could tune charge transport and capacitance (for example, CNO Vox 1150 exhibits lower σ_{dc} and ϵ_s values compared with those of ND Vox and CNO Vox 1650).

3.3. Electrochemical Properties of CNOs

CNO electrodes exhibit electrochemical behavior characteristic of porous electric double-layer capacitors (EDLCs): the measured capacitance is dominated by non-Faradaic double-layer charging, and the cyclic voltammograms (CVs), especially at low scan rates, approach an almost rectangular profile, which is the canonical signature of fast, reversible EDL charging with minimal kinetic limitations and only minor resistive distortion. This interpretation is consistent with the established CV response of an ideally capacitive interface, where the current scales quasi-linearly with scan rate and the current–potential trace remains rectangular unless appreciable ohmic drop or ion-transport limitations distort the shape.^{45,46} For electrochemical measurements, dispersions of CNOs or NDs in EtOH (2 mg mL^{−1}) were drop-cast onto GCEs (0.012 mg per electrode). The modified electrodes were tested in aqueous solution containing 0.1 M supporting electrolyte (NaCl, NaClO₄, LiClO₄, or (Et₄)NCl); the resulting films remained mechanically and electrochemically stable throughout cycling (−100 and +500 mV vs Ag/AgCl, Figures S3–S5). Annealing at 1,650 °C increases graphitization and electronic connectivity, producing faster charge storage and more ideal electric double-layer (EDL)

behavior for all CNO 1650 materials (Figures S3–S5, red curves). The CV curves, particularly at low scan rates, approach a nearly rectangular shape, which is the canonical signature of rapid, reversible EDL charging with minimal kinetic limitations and small resistive distortion. The high reversibility, stable cycling, and absence of redox peaks within the applied potential window indicate predominantly capacitive storage with a negligible Faradaic contribution and no detectable chemical transformations under these conditions.⁴⁷ Deviations from an ideal rectangular response are therefore most consistently attributed to resistive or ion-transport effects rather than changes in the charge-storage mechanism.

To complement the electrochemical observations, we assess charge transport directly using BDS, which quantifies the intrinsic conductivity of the carbon framework over broad frequency and time scales. Compared with electrochemical impedance spectroscopy (EIS), BDS is less sensitive to electrode wetting, separator/contact artifacts, and equivalent-circuit assumptions, and thus provides a more materials-intrinsic view of electronic transport. It is particularly relevant for curvature-rich, percolating CNO networks, as the framework's conductivity directly governs series (layer) resistance in EDLC operation. In line with established EDLC analyses, conductive porous carbons with accessible porosity are expected to exhibit low internal resistance and minimal resistive losses when electronic pathways are well percolated and pore architecture supports efficient ion transport.^{45,46} Consistent with these precedents and with the nearly rectangular CVs observed here, the BDS results provide sufficient support for the conductivity comparison and the structure–property interpretation; therefore, additional EIS measurements are not essential for the mechanistic conclusions presented.

The specific capacitance (C_s) of all CNO electrodes exceeds that of ND electrodes, consistent with the more conductive, defect-rich, and accessible microstructure of CNOs, which facilitates ion and electron transport (Figures S3–S5). C_s was calculated from CV by integrating the total charge over the whole cycle and normalizing by scan rate, mass loading, and potential window:

$$C_s = \frac{\int_{E_1}^{E_2} i(E) dE}{2\nu m(E_2 - E_1)} \quad (1)$$

where E_1 , E_2 are the cutoff potentials in CV; $i(E)$ is the instantaneous current; $i(E)dE$ is the total voltammetric charge obtained by integration of the positive and negative sweeps in the CVs; ν is the scan rate; and m is the mass of the individual sample (0.012 mg). C_s of ND and CNO electrodes was calculated using eq 1, which is summarized in Table 2, where the effect of the supporting electrolyte on the electrochemical properties of CNOs and NDs was investigated. The C_s values obtained from CVs at 10 mV s^{−1} in 0.1 M supporting electrolytes reveal a clear dependence on the electrochemical properties of NDs and CNOs, as well as the supporting electrolyte. For all systems, the transformation of NDs into CNOs results in a pronounced increase in C_s , reflecting the progressive increase in surface area, graphitization, and conductivity upon annealing. This interpretation aligns with the EDLC literature, in which near-rectangular voltammograms and the absence of redox peaks are taken as signatures of fast, reversible double-layer charging with minimal Faradaic contribution.^{45,46} In the Molto and Amine series, C_s increases monotonically with thermal treatment, from ca. 4–15 F g^{−1} for the ND and CNO 1150

Table 2. C_s Values Calculated Based on CVs Using eq 1 for NDs and CNOs at a Scan Rate of 10 mV s^{−1}

Materials	Specific capacitance, C_s (F g ^{−1})			
	NaCl	NaClO ₄	(Et ₄ N)Cl	LiClO ₄
ND Molto	4.3	5.5	27.9	8.7
CNO Molto 1150	14.7	14.8	77.7	24.2
CNO Molto 1650	32.9	17.9	155.4	91.0
ND Amine	3.8	8.2	2.1	36.7
CNO Amine 1150	14.7	9.9	62.1	99.0
CNO Amine 1650	38.9	25.7	93.1	136.5
ND Vox	3.6	1.0	2.4	4.8
CNO Vox 1150	8.4	9.2	9.7	15.4
CNO Vox 1650	22.3	25.8	75.9	36.1

samples to ca. 33–39 F g^{−1} for CNO 1650 in NaCl. The effect is most potent in (Et₄N)Cl and LiClO₄, where CNO Molto 1650 achieves 155.4 and 91 F g^{−1}, and CNO Amine 1650 achieves 93.1 and 136.5 F g^{−1}, respectively, significantly higher than their ND precursors. Among the materials, the CNO Molto and CNO Amine series exhibit the most favorable balance between electrical conductivity and surface functionality, while CNO Vox samples, despite higher oxygen content, display lower capacitances (≤ 76 F g^{−1} at 1,650 °C), attributable to structural disorder and disrupted π conjugation of graphitic layers. However, these values compare favorably with those reported for other graphitic CNOs (80–150 F g^{−1}) and heteroatom-doped onion-like carbons (120–200 F g^{−1}) in similar electrolytes,⁴⁸ supporting the conclusion that the combination of optimized onion-shell architecture and controlled surface chemistry enables efficient charge storage.

It should be noted that, consistent with community reporting guidance for EDLC, gravimetric capacitance (F g^{−1}) is the most meaningful primary metric for porous carbon powders, because converting C_s into an electrochemical surface area (ECSA), via a presumed areal C_s implicitly assumes a unique, transferable capacitance-per-area and a uniquely defined accessible area, assumptions that are demonstrably invalid for nanoporous carbons, where C_s is strongly structure- and electrolyte-dependent.^{49–51} Moreover, capacitance-derived ECSA is not necessarily proportional to the ORR-relevant active centers (defects or curvature-activated sites), and the methodological ambiguity of inferring ECSA from EDLC, especially for nanoporous electrodes, is explicitly emphasized in recent critical analyses.^{52,53} Accordingly, we report C_s in gravimetric units (F g^{−1}) for the SC-relevant discussion and interpret ORR activity through kinetic/selectivity descriptors (RRDE metrics) rather than C_{dl} -derived “specific activity,” thereby maintaining mechanistic clarity for these heterogeneous, porous carbon nanocatalysts.

The gradual transformation from NDs to CNOs leads to an increase in the specific surface area (S_{BET}) and electrical conductivity, accompanied by enhanced graphitization. S_{BET} rises from 285 m² g^{−1} for ND Molto to 454 m² g^{−1} for CNO Molto 1650, and from 261 to 383 m² g^{−1} for ND Amine and CNO Amine 1650, respectively, paralleling a pronounced increase in C_s . The C_s scales with S_{BET} and conductivity, reaching 155.4 F g^{−1} for CNO Molto 1650 in (Et₄N)Cl and 136.5 F g^{−1} for CNO Amine 1650 in LiClO₄, consistent with the development of concentric graphenic layers that provide extensive, accessible interfaces for charge storage and transport. The correlation between C_s and S_{BET} is nonlinear, consistent with prior reports for porous carbons.^{54,55} At high porosity,

additional increases in S_{BET} yield diminishing improvements in C_s due to limited ion accessibility and confinement effects.^{56,57} Thus, optimal C_s is achieved when a high S_{BET} is coupled with an appropriate pore size distribution, sufficient electrical conductivity, and compatible electrolyte ion size (Table S4). The combined influence of Stokes radius (r_s), hydrated radius (r_h), and standard molar enthalpy of hydration ($\Delta H_{\text{hyd}}^\circ$) underscores the critical role of electrolyte-electrode matching in determining overall charge storage efficiency (Table S4). The electrolyte dependence follows the sequence $(\text{Et}_4\text{N})\text{Cl} > \text{LiClO}_4 > \text{NaClO}_4 \approx \text{NaCl}$ (Tables 2 and S4), consistent with the mobility and hydration characteristics of the ionic species. Electrolytes containing large, weakly hydrated ions such as $(\text{Et}_4\text{N})^+$ ($r_h = 0.400$ nm, $\Delta H_{\text{hyd}}^\circ = -154.9$ kJ mol⁻¹)⁵⁸ and ClO_4^- ($r_h = 0.338$ nm, $\Delta H_{\text{hyd}}^\circ = -165.3$ kJ mol⁻¹)⁵⁹ promote facile desolvation and deeper penetration into mesoporous, graphitic domains of the electrodes. In contrast, smaller, highly hydrated ions such as Na^+ and Li^+ ($r_h = 0.358$ and 0.382 nm; $\Delta H_{\text{hyd}}^\circ = -240$ and -279 kJ mol⁻¹, respectively)⁶⁰ experience higher energy barriers to interfacial transfer, which limits their C_s values. This trend corroborates earlier findings that ion–electrode compatibility, particularly hydration dynamics and desolvation energy (ions must dehydrate to enter micropores effectively), governs double-layer formation and C_s .⁶¹ This trend underscores the crucial role of ion-electrode compatibility: bulky, weakly solvated cations form efficient EDLs on curved sp²-hybridized carbon surfaces, aided by favorable ion- π interactions and high conductivity within the graphitized layers of the CNOs.

XPS analysis reveals that the conversion of NDs into CNOs is accompanied by a significant enrichment of sp²-hybridized carbon (up to 81.8 at. % for CNO Molto 1650), confirming the formation of well-ordered, conductive graphitic domains. The presence of N- and O-containing groups modulates the electronic and interfacial properties of the materials. CNO Molto, characterized by high sp²-hybridized C atom content and moderate oxygen levels (2–4.8 at. %), exhibits excellent conductivity and efficient electron delocalization through π - π^* conjugation. CNO Amine retains N functionalities, mainly pyridinic and graphitic N, providing basic and electronically active sites that facilitate ion adsorption and enhance interfacial polarization. CNO Vox, in contrast, contains the highest O content (up to 10.6 at. % at 1,150 °C), dominated by quinone, phenolic, and ether-like species that increase surface polarity but disrupt π conjugation, resulting in lower conductivity and C_s . The N and O functionalities further tune the electronic and interfacial behavior: CNO Molto, with high sp²-hybridized C atom content and low O levels (2–4.8 at. %), shows optimal electron delocalization through π - π^* conjugation; CNO Amine retains pyridinic and graphitic N species that contribute basic and electroactive sites for ion adsorption; whereas CNO Vox, containing the highest O concentration (up to 10.6 at. %), exhibits lower conductivity and C_s due to disrupted π conjugation and charge trapping at oxygenated defects. These findings reinforce that both graphitization and heteroatom configuration directly modulate the charge transport and storage mechanisms in CNO electrodes.

The electrochemical data establish a direct structure–property–electrolyte relationship: graphitization and heteroatom-controlled surface chemistry dictate the conductivity and C_s . At the same time, r_h and $\Delta H_{\text{hyd}}^\circ$ govern the accessibility of the ions within the carbon network. The effect of large accessible surface area, high electrical conductivity, and N surface functionality renders CNO Molto 1650 and CNO Amine

1650 the most effective electrodes, achieving superior charge storage and electrochemical response across all tested electrolytes. This trend underscores the crucial role of ion-electrode compatibility: bulky, weakly solvated cations form efficient EDL on curved sp²-hybridized C surfaces, aided by favorable ion- π interactions and high conductivity within the graphitized layers of the CNOs.

3.4. Electrocatalytic Properties of CNOs

CNOs and NDs were evaluated as OR electrocatalysts using RRDE, with commercial Pt/C and two other carbon nanostructures serving as benchmarks under identical conditions. CNOs were synthesized by pyrolysis at 1,150 °C and 1,650 °C to probe the influence of graphitization temperature on OR reaction (ORR) activity and selectivity. Catalyst inks were drop-cast onto polished Pt/glassy-carbon (Pt/GC) electrodes to form uniform thin films. RRDE measurements were performed in an O₂-saturated solution containing the supporting electrolytes (0.1 M KOH and H₂SO₄) at different rotational speeds of RRDE using linear sweep voltammetry (LSV). The ring was held at an oxidative potential to quantify H₂O₂, and the collection efficiency (N) was calibrated before testing. From the disk and ring currents, the electron-transfer number (n) was obtained in both media, enabling direct comparison of CNOs (pyrolyzed at 1,150 °C vs 1,650 °C) and NDs against Pt/C, in terms of onset potential, limiting current density, Tafel slope, and 2e⁻/4e⁻ selectivity (please see SI, Figures S7–S13, Tables S1–S4). This protocol enables us to correlate the synthesis temperature-dependent structural features of CNOs and their surface chemistry with NDs, as well as ORR kinetics and pathways, in both alkaline and acidic environments. Because the catalysts are deposited as porous thin films, the reported Tafel slopes (and the derived transfer coefficient α) are treated below as apparent layer-level diagnostics rather than intrinsic kinetic constants of an electrode interface.

For a planar smooth disk electrode, the diffusion-convection limiting current density (J_{O}) at the disk of the RRDE electrode reaction can be described by the Koutecký–Levich (K–L) equation:⁶²

$$\frac{1}{J_{\text{d,O}}} = \frac{1}{J_{\text{k,O}}} + \frac{1}{0.201nFD_{\text{O}}^{2/3}\nu^{-1/6}\omega^{1/2}C_{\text{O}}^{\circ}} \quad (2)$$

where $J_{\text{d,O}}$ is the measured oxidant reduction current density (A cm⁻²); $J_{\text{k,O}}$ is the electron-transfer kinetic current density (A cm⁻²); n is the electron-transfer number (dimensionless); F is Faraday's constant (96,487 A s mol⁻¹); D_{O} is the diffusion coefficient of the oxidant (cm² s⁻¹); ν is the solution kinematic viscosity (cm² s⁻¹); ω is the electrode angular rotation rate (rad s⁻¹); C_{O}° is the bulk concentration of the oxidant (mol cm⁻³). For nonlimiting diffusion conditions, the disk electrode current density ($J_{\text{d,O}}$) would be

$$J_{\text{d,O}} = 0.201nFD_{\text{O}}^{2/3}\nu^{-1/6}\omega^{1/2}(C_{\text{O}}^{\circ} - C_{\text{O}}^{\text{s}}) \quad (3)$$

where C_{O}^{s} is the disk surface concentration of the oxidant (mol cm⁻³).

Although the K–L analysis is rigorously derived for a smooth, planar electrode under well-defined hydrodynamic boundary conditions, its direct use becomes increasingly ambiguous for porous, high-surface-area carbon catalyst layers.⁶² In such films, the measured disk current reflects not only interfacial charge-transfer kinetics but also distributed ionic/electronic resistances

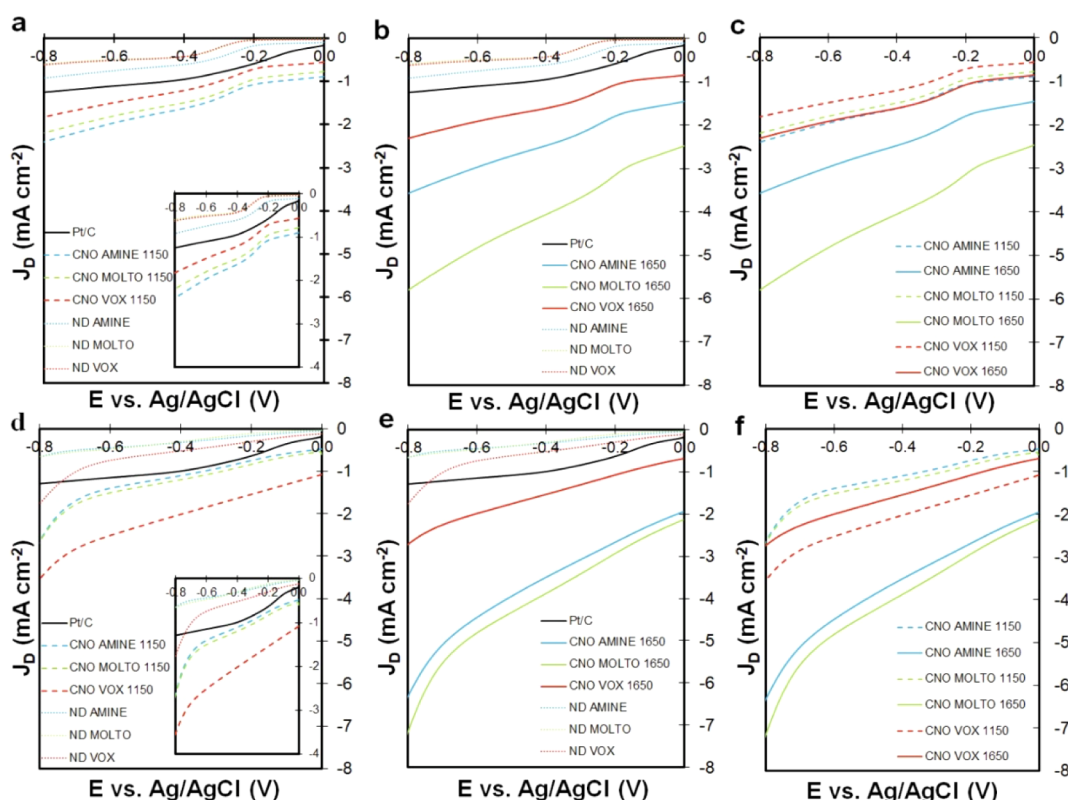


Figure 8. LSV curves for different CNOs and Pt/C in O_2 -saturated (a–c) 0.1 M KOH; (d–f) 0.1 M H_2SO_4 with a scan rate of 10 mV s^{-1} at 1,000 rpm.

across the catalyst layer, nonuniform local overpotential within pores and along the layer thickness, internal O_2 transport limitations not captured by the external layer, and potential-dependent site wetting. These factors violate the key assumption that the electrode behaves as a nonporous interface with mass transport dominated by the external convective-diffusive boundary layer. Consequently, kinetic currents inferred from single-condition K–L corrections (or any approach that relies on a poorly defined limiting plateau in a porous film) should be interpreted as effective, model-dependent parameters rather than intrinsic kinetic descriptors (see the SI). This limitation is not merely practical but mechanistic: porous-electrode theory predicts that apparent α and apparent Tafel slopes can deviate substantially from their intrinsic values when the reaction occurs within porous structures.^{63,64} In particular, Soderberg et al. showed that long and narrow pores, finite ionic/electronic conductivity, and nonuniform porous-film properties can yield apparent $\alpha < 0.5$ (often near 0.25) even when the intrinsic charge-transfer symmetry is conventional.⁶⁵

CNOs, which are composed of concentric, positively curved graphenic layers, provide a prototypical high-curvature sp^2 -hybridized carbon scaffold in which local Gaussian curvature is intrinsically significant due to their small radii and “dense layers packing”.¹⁸ In an alkaline medium (0.1 M KOH), both NDs and CNOs displayed onset potentials of approximately -0.2 V (Figure 8a–c). The nonzero current at the start of the LSV curves is attributed to systematic background contributions, dominated by double-layer capacitive charging and minor residual faradaic currents, which are commonly observed for nanostructured electrodes.^{66,67} Because all measurements were performed under identical conditions (electrode preparation, electrolyte, scan rate, and cell configuration), this baseline offset is consistent across samples and does not affect the comparative

analysis; the performance metrics are evaluated in the relevant potential region rather than at the initial baseline. Similar LSV baseline offsets have been widely reported.⁶⁷

NDs exhibited the lowest $J_{d,0}$ at the onset potential, whereas CNOs demonstrated superior activity. Within the CNOs formed at $1,150^\circ\text{C}$, CNO Amine 1150 delivered -1.07 mA cm^{-2} at the onset potential and the highest maximum $J_{d,0}$ of -2.40 mA cm^{-2} . This performance correlates with its higher N atom content (Tables S5–S7), introducing pyridinic- and graphitic-N that (i) modulates local charge density on adjacent C sites, (ii) stabilizes $*OOH/*O$ intermediates, and (iii) lowers charge-transfer resistance across the film. By contrast, in the $1,650^\circ\text{C}$ series, CNO Molto 1650 stands out, reaching a $J_{d,0}$ value of -3.14 mA cm^{-2} at the onset potential and -5.80 mA cm^{-2} at the limiting region.

At higher temperatures, the heteroatom content is reduced through thermal dedoping, and the electrocatalytic response becomes governed by curvature-stabilized defect domains and graphitic ordering. These factors yield faster ORR kinetics and higher achievable currents. Consequently, CNOs treated at $1,650^\circ\text{C}$ consistently outperform both the $1,150^\circ\text{C}$ analogues and the commercial Pt/C benchmark under the same conditions (Figure S8), underscoring a transition from dopant-controlled activity at $1,150^\circ\text{C}$ to defect- and ordering-controlled activity at $1,650^\circ\text{C}$.

In an acidic medium (0.1 M H_2SO_4), the ORR trends closely follow the interplay among curvature-induced electronic structure, defectiveness, and surface chemistry. Among the $1,150^\circ\text{C}$ materials, CNO Vox 1150 was the only $1,150^\circ\text{C}$ material to match the performance of Pt/C, achieving a maximum $J_{d,0}$ of -3.55 mA cm^{-2} (Figure 8d), which we attribute to a favorable combination of curved structures, defects, and a moderate level of oxygen functionalities that

balance active-site density with sufficient conductivity. Consistent with the alkaline results, CNOs obtained at 1,650 °C exhibited significantly higher $J_{d,O}$ in acids (Figure 8f). By contrast, other 1,150 °C CNOs likely retain a higher fraction of sp^3 -like carbon and nonconductive oxygen functionalities; these defects increase the site count but penalize electron transport and site utilization in strongly protonic media, thereby limiting current. Specifically, CNO Amine 1650 and CNO Molto 1650 reached maximum $J_{d,O}$ values of -6.34 and -7.19 mA cm $^{-2}$, respectively (Figure 8d). In acidic electrolyte (0.1 M H $_2$ SO $_4$), the ORR trends track the defectiveness and surface chemistry of the CNOs.

Raising the synthesis temperature to 1,650 °C increases graphitic order and lowers intergranular resistance, while a subset of curvature-stabilized defects and heteroatom sites survives or transforms into more catalytically competent configurations (pyridinic- and graphitic-N sites, Tables S5–S7). In line with this, CNO Amine 1650 and CNO Molto 1650 deliver markedly higher $J_{d,O}$ values of -6.34 and -7.19 mA cm $^{-2}$, respectively, well above both the 1,150 °C series and Pt/C (Figure 8e). We ascribe the improvement to (i) enhanced through-plane conductivity that improves kinetic current and mass-transport utilization, (ii) persistence of defect-rich domains that bind O $_2$ /OOH* with suitable energetics in acid, and (iii) in the “Amine” series, thermally induced conversion of surface amines (NDs Amine) to pyridinic- and graphitic-N sites (defects), which are known to stabilize ORR intermediates in acidic media. The data indicate that defect engineering is necessary but not sufficient: maximal ORR performance in acid emerges when defect-derived active sites are embedded within a sufficiently graphitized, well-connected CNO network, achieved here at 1,650 °C. In contrast, excessive disorder at 1,150 °C compromises electronic pathways and suppresses the attainable current, despite nominally higher defect densities.

We performed additional studies on representative metal-free carbon catalysts (mesoporous carbon and graphitic carbon nitride) under identical alkaline conditions (0.1 M KOH; Figure S8), which highlight a clear performance hierarchy: Pt/C remains the highest-performing reference, whereas conventional low-curvature carbon materials deliver comparatively low ORR current densities and less favorable onset potentials. This outcome is consistent with prior mechanistic analyses showing that, in the absence of atomically dispersed metal centers, planar carbon frameworks often rely on a limited population of intrinsic defects to activate O $_2$, which constrains kinetic current and shifts the onset to higher overpotentials.⁶⁸ In contrast, the CNO-based catalysts evaluated here exhibit substantially enhanced ORR activity (higher current densities and more positive onset potentials than the planar carbon structures and Pt/C), indicating that the CNOs provide a larger density of catalytically competent sites and more favorable adsorption energetics for oxygenated intermediates in alkaline electrolyte (Figure S8). The superior performance of CNOs is readily interpretable through curvature-driven electrocatalysis.^{68,69} High surface curvature introduces local strain, a high density of nonhexagonal rings, and rehybridized carbon (mixing of sp^2 - and sp^3 -hybridized C atoms) relative to planar graphene-like domains, features that collectively perturb the electronic structure and can strengthen or optimize O $_2$ /OOH* binding and charge transfer at carbon sites.⁶⁹ This mechanistic picture aligns with the broader curvature–activity framework articulated for the ORR, where “surface curvature” is predicted and observed to modify adsorption scaling relations and reaction barriers, thereby

improving electrocatalytic activity compared with low-curvature carbon analogues. The present comparative data support the conclusion that CNO curvature generates a catalytically more active carbon microenvironment than mesoporous or graphitic carbon nitride (Figure S8), consistent with prior reports of single- (C $_{60}$) or multilayered fullerenes (CNOs) showing higher catalytic activity than planar CNs.⁶⁸

Because CNO Molto 1650 and CNO Amine 1650 showed the best electrocatalytic performance in these studies (Figure S8), their electrochemical stability was evaluated in the two 0.1 M supporting electrolytes subsequently used for CNO electrocatalysis: H $_2$ SO $_4$ and NaOH (Figure S6). Long-term cycling stability was performed by CV for 10,000 cycles within -0.50 to $+0.50$ V vs Ag/AgCl at 300 mV s $^{-1}$. Both CNOs exhibit high stability, with only a moderate C_s value decrease, indicating that the multilayered, highly graphitized CNO's architecture remains electrochemically stable under repeated polarization in both media. Quantitatively, CNO Amine 1650 shows particularly robust retention, preserving $\sim 94\%$ of its initial C_s in H $_2$ SO $_4$ and $\sim 89\%$ in NaOH after 10,000 cycles, consistent with a well-connected sp^2 -hybridized C framework and stable N-derived surface sites that tolerate repeated charging/discharging. CNO Molto 1650 starts from a higher C_s value (reflecting its larger accessible surface and conductivity) and remains comparatively stable over most of the protocol; however, it exhibits a more substantial late-stage decline in alkaline electrolyte ($\sim 94\%$ to 8,000 cycles), retaining $\sim 76\%$ in NaOH (up to 8,000 cycles) vs $\sim 86\%$ in H $_2$ SO $_4$ at 10,000 cycles. These results confirm that the top-performing CNOs are not only catalytically active but also sufficiently stable in both acidic and alkaline supporting electrolytes, supporting their applicability for subsequent ORR and related electrocatalytic measurements under the same electrolyte environments.

We evaluated the polarization data using a conventional Tafel formalism (Figure S13), $E = a + b \log |j_D|$, from which the cathodic transfer coefficient follows $\alpha = 2.303RT/(F|b|)$ (please see the SI). For an activation-controlled process at an equipotential interface, α and j_D are meaningful kinetic parameters, and b is expected to be constant over a sufficiently wide current range. In contrast, all three analyzed data sets for CNO Molto, CNO Amine, and CNO Vox (CNOs obtained at 1,650 °C) yield vast apparent Tafel slopes in the E vs $\log |j_D|$ representation ($|b| \approx 2.0$ – 2.6 V dec $^{-1}$; 2000–2600 mV dec $^{-1}$), corresponding to very small transfer coefficients ($\alpha \approx 0.02$ – 0.03 at room temperature, 25 °C). Representative best-fit windows gave $\alpha \approx 0.0235$ (CNO Molto, Table S1), 0.0238 (CNO Amine, Table S2), and 0.0238 (CNO Vox, Table S3), while full-range fits remained on the same order ($\alpha \sim 0.025$ – 0.030). Such values are far below the range expected for elementary charge-transfer control at a nonporous interface and, therefore, indicate that the measured slopes are dominated by porous-layer effects rather than intrinsic ORR kinetics. Consistent with this interpretation, van der Heijden et al. proposed the Tafel slope plot as a diagnostic to distinguish kinetic from nonkinetic contributions and emphasized that a horizontal region is a practical prerequisite for assigning a meaningful single Tafel slope; otherwise, the reported slope becomes a window-dependent average influenced by transport, ohmic losses, and porosity of the catalyst-layer.⁷⁰ For nanoporous CNO electrodes, the “apparent” Tafel slope and transfer coefficient (α) extracted from a conventional η – $\log |j|$ plot should be treated primarily as diagnostic parameters (Figure S13, Tables S5–S7), not intrinsic kinetic constants, because the measured polarization response

generally reflects coupled interfacial charge transfer and transport inside the porous catalyst layer rather than Butler–Volmer kinetics at a uniform potential. Porous electrodes can exhibit spatially varying local overpotentials caused by ionic resistance, potential gradients, reactant depletion, and nonuniform wetting, which mathematically yield an effective (apparent) α that differs from the intrinsic value even when the elementary-step physics remains unchanged. This limitation is well established: porous-electrode properties alone can shift the measured α and distort mechanistic interpretation,⁶⁵ and catalyst-layer microstructure (ionomer distribution, porosity, thickness, tortuosity) can measurably change the observed ORR Tafel slopes in nominally identical materials.⁷¹ More broadly, several recent analyses caution that “standard electrokinetic analysis” often fails on nanostructured active electrodes because the basic assumption of a single, well-defined interfacial driving force is violated when catalyst layers introduce internal transport artifacts.⁷² Therefore, for high-curvature, heteroatom-doped nanoporous carbons, extensive apparent slopes (and correspondingly nonphysical α values) are most consistently interpreted as signatures of extrinsic limitations rather than a change in the intrinsic rate-determining step.^{70,73–75}

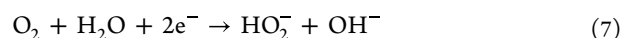
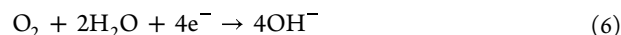
The H₂O₂ selectivity analysis (RRDE ring current) is particularly valuable because it is less sensitive than the Tafel plot and determination of α to the lack of a well-defined kinetic region in the disk polarization curve; therefore, selectivity trends are emphasized here as the primary mechanistic indicator, while the Tafel plot analysis is reported only as a diagnostic for nonkinetic contributions. Figure 9 shows the percentage of ORR

$$n = \frac{4i_d}{i_d + \frac{i_r}{N}} \quad (5)$$

where i_r and i_d represent the ring and disk currents (A), respectively. N is the collection efficiency of the RRDE (dimensionless), which depends on the electrode radius (in our study, 0.26), and n is the number of electrons transferred per molecule of O₂ during ORR (dimensionless). The %HO₂[−] further supports a curvature-mediated picture in both electrolytes (0.1 M KOH and H₂SO₄). The H₂O₂ selectivity decreases monotonically with decreasing potential, consistent with a transition from outer-sphere to inner-sphere ORR kinetics as adsorption strengthens and the 4e[−] pathway becomes favored.

Across most materials and potentials (Figures 9a, b, and S7a and S7b), H₂O₂ fraction remains low, ~3.3–8.6%, which corresponds to $n \sim 3.9$ –3.97, indicating a dominantly 4e[−] reduction to water (or OH[−]) with only a minor 2e[−] pathway. A notable exception is CNO Molto 1150 in an alkaline medium (Figure 9a), which exhibits the highest H₂O₂ selectivity at the most positive potentials, reaching 16.3%. We attribute this to OH[−] preadsorption on more defective graphitized CNO's layers that weakens O₂ chemisorption and promotes outer-sphere electron transfer, increasing the probability of the 2e[−] route to H₂O₂ at high potentials (eq 6, peroxide (2e[−] path)).^{77,78}

As the potential shifts negative, enhanced O₂ adsorption and carbon-defective sites drive convergence toward the 4e[−] pathway, reducing H₂O₂ output (eq 6, alkaline ORR overall (4e[−] pathway)):



Linking the selectivity to the defectiveness of the carbon surface, the trends are consistent with the structural evolution observed during thermal treatment across nanostructures. Lower-temperature CNOs (1,150 °C) possess higher densities of defects and oxygenated terminations (quinone, carbonyl, phenolic), which can act as mediator sites that favor 2e[−] H₂O₂ formation, especially under conditions where adsorption is weak (high potentials) and electron transfer proceeds more outer-sphere. More highly annealed CNOs (1,650 °C), by contrast, combine high curvature with improved graphitization and conductivity while still retaining a population of catalytically competent defect domains and lower charge-transfer resistance; this combination supports stronger inner-sphere O₂ adsorption and efficient proton/electron delivery to *OOH, thereby biasing the 4e[−] route and minimizing H₂O₂ over the entire potential window.

The NDs, with their predominantly sp³ cores and limited graphitic domains, generally show lower %HO₂[−] than the CNOs at 1650 °C at comparable potentials, consistent with fewer extended sp² edge sites and greater charge-transfer resistance; nevertheless, their H₂O₂ fractions remain mostly within the same low range (3.3–8.6%), giving n values close to 4. The RRDE data indicate that optimally graphitized yet defect-accessible CNOs, as achieved at 1,650 °C, maximize ORR activity while maintaining low H₂O₂ selectivity. In contrast, more defective, less ordered carbons (e.g., CNO Molto 1150) transiently promote the 2e[−] route. The RRDE polarization curves (Figures S9 and S10) exhibit diffusion-controlled current regions characteristic of ORR, and a gradual increase in $J_{d,O}$ is observed at higher rotation speeds of the RRDE, as expected for electrocatalysis. The more pronounced $J_{d,O}$ obtained for

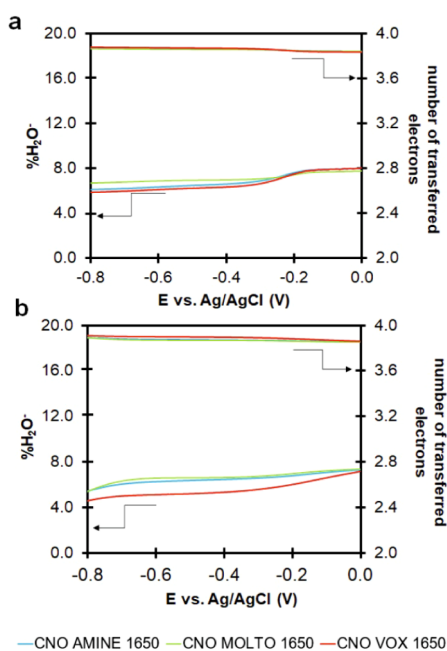


Figure 9. %HO₂[−] and the number of transferred electrons for different CNOs obtained at 1,650 °C in (a) 0.1 M KOH or (b) H₂SO₄ at 1,000 rpm.

proceeding via the H₂O₂ pathway at a rotation rate of 1,000 rpm, as well as the ORR electron number (n) calculated from the total RRDE currents using eqs 4 and 5:⁷⁶

$$\% \text{HO}_2^- = 100 \times \frac{i_r/N}{i_d + i_r/N} \quad (4)$$

nanostructures annealed at 1,650 °C compared to those pyrolyzed at 1,150 °C indicates enhanced mass transport and improved electrochemical activity. Similar trends have been reported for carbon nanomaterials subjected to high-temperature treatment, where increased graphitization promotes more efficient charge transfer and O₂ adsorption.⁷⁹ The corresponding K–L plots (Figures S11 and S12) display nearly linear behavior, suggesting a mixed kinetic-diffusion control of the ORR process. The parallel slopes of the K–L plots over the investigated potential range confirm a consistent electron-transfer pathway.⁸⁰ For most of the materials, the calculated number of transferred electrons is close to 4, indicating that the ORR proceeds predominantly through the desirable 4e[−] pathway leading to the direct formation of OH[−] ions. This result is consistent with previously reported results (Figures 9 and S7) and is characteristic of efficient ORR electrocatalysis in both alkaline and acidic media.⁸¹

To further contextualize the RRDE trends within the curvature-engineering framework, it is essential to emphasize that CNOs represent a structurally well-defined class of positively curved sp²-hybridized carbon frameworks, in which the local Gaussian curvatures are intrinsically high due to their small radii and concentric-shell packing.⁸² Such curvature forces carbon pyramidalization (σ – π mixing) and induces local polarization, both of which are expected to perturb frontier electronic states and interfacial electric fields, thereby modulating adsorption energetics for ORR intermediates and favoring inner-sphere pathways relative to planar graphitic surfaces.⁸³ These concepts are supported by theoretical and computational studies showing curvature-induced polarization in CNs and curvature-dependent oxygen adsorption on nanotubes versus graphite.⁸⁴ Moreover, the geometric connection between local pyramidalization and Gaussian curvature provides a quantitative descriptor for rationalizing why defect motifs become energetically stabilized and chemically active on curved carbon lattices,⁸⁵ consistent with recent syntheses of curvature effects in carbon electrocatalysis.⁸⁶ In our data, this curvature-driven electronic tuning manifests as a temperature-dependent shift from dopant-dominated activity (CNOs obtained at 1,150 °C) to an optimized balance of conductivity and curvature-stabilized active site motifs (CNOs obtained at 1,650 °C). The 1,650 °C CNOs consistently deliver higher disk currents and maintain low H₂O₂ selectivity ($n \approx 4$) in both alkaline and acidic electrolytes, indicating efficient 4e[−] reduction enabled by (i) improved through-layer charge transport and (ii) a surviving population of catalytically competent defects embedded in a well-connected sp²-hybridized network. Conversely, the more disordered 1,150 °C materials can transiently favor the 2e[−] route at high potentials (e.g., elevated H₂O₂ selectivity for CNO Molto 1150 in alkaline medium). These results align with an established mechanistic understanding of the ORR for metal-free carbon catalysts, where activity and selectivity depend on the interplay among defect topology, heteroatom speciation, and electronic transport, and they substantiate curvature engineering as a practical lever to maximize intrinsic kinetics while suppressing peroxide formation.

4. CONCLUSIONS

Curvature engineering, implemented here by thermally converting functionalized NDs into CNOs, offers a practical strategy to tune carbon hybridization (sp²- and sp³-hybridized C atoms), defect topology, and heteroatom chemistry, thereby

improving both charge transport and ORR performance. Using the Kuznetsov annealing protocol at 1,150 °C and 1,650 °C, we observe a clear temperature-driven structural evolution: at 1,150 °C, the materials remain partially converted ND–CNO core–shell hybrids with higher N and O atom contents and substantial disorder, whereas annealing at 1,650 °C yields near-complete transformation into quasi-spherical, multilayered CNOs with predominantly turbostratic sp²-hybridized C atoms, reduced heteroatom content, and markedly improved electronic connectivity. HRTEM and XRD confirm the transition from ND cores to concentric graphitic layers (including a broadened (002) reflection). At the same time, XPS and STEM-EDX show increased sp²-hybridized C fractions (up to 82 at. % for CNO Molto 1650), retention of precursor-derived dopants as distinct N and O chemical environments, and uniform dopant distributions. Thus, the pyrolysis temperature serves as a single control parameter that jointly governs conversion extent, layer continuity, defect density, and dopant speciation, defining the electronic structure and accessibility of electroactive sites in CNOs.

This structural control directly translates to electrochemical performance. The CNOs obtained at 1650 °C (CNO Molto and CNO Amine) exhibit higher dc conductivity and increased dielectric response relative to their ND precursors, consistent with percolation through a well-connected sp²-hybridized carbon network and enhanced interfacial polarization in multilayered fullerenes. Their high C_s values (155 and 137 F g^{−1}, respectively) reflect the combined effects of conductive frameworks, accessible porosity, and efficient ion transport; weakly hydrated bulky ions ((Et₄N)⁺ and ClO₄[−]) further increase pore utilization and EDL formation.

RRDE measurements in 0.1 M KOH and H₂SO₄ benchmarked NDs and CNOs against Pt/C and low-curvature carbon references, enabling the simultaneous evaluation of ORR activity and H₂O₂ selectivity. Because these catalysts operate as nanoporous films, K–L corrections and Tafel-derived parameters are treated as apparent, layer-level diagnostics rather than intrinsic interfacial kinetics, given that internal resistances, nonuniform local overpotentials, and intralayer O₂ transport can dominate the observed polarization behavior. Within this interpretation, the data resolve a “defect paradox”: although the 1150 °C materials are more defect-rich, excessive disorder degrades electronic transport, limiting attainable ORR currents and selectivity. Maximal performance is achieved when curvature-stabilized defects and N-derived motifs are embedded in a sufficiently graphitized, well-connected sp² network, as realized at 1,650 °C. Consistent with a curvature-mediated mechanism, where positive curvature enforces pyramidalization (σ – π mixing) and local polarization that tunes adsorption energetics, the CNOs (1650 °C) maintain predominantly 4e[−] ORR in both electrolytes ($n \approx 4$; low H₂O₂ selectivity), whereas the more disordered CNOs (1,150 °C) can transiently increase H₂O₂ formation at high potentials. Overall, these results establish a processing-structure–property map demonstrating that high-temperature, ND-derived CNOs provide a stable, metal-free platform that combines improved charge transport with high ORR activity and suppressed H₂O₂ formation. The results motivate future optimization by targeted control of N speciation and porosity, while avoiding strongly oxidizing surface functionalities in CNOs.

■ ASSOCIATED CONTENT

Data Availability Statement

The raw data (electrocatalysis, XPS, HRTEM-STEM) are available in the Zenodo repository under the title “<Defects, doping, and curvature of CNOs for ORR electrocatalysis>” and can be accessed at <Zenodo DOI link, <https://doi.org/10.5281/zenodo.18909362>>.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.5c05570>.

HRTEM images of CNOs derived from NDs at 1,150 and 1,650 °C. CVs of Molto-, Amine-, Vox-derived CNs (NDs and CNOs) in the different supporting electrolytes. RRDE studies (LSVs, Koutecký-Levich, and Tafel plots) in acidic and basic solutions at various rotation speeds and various potentials. XPS C 1s, N 1s, and O 1s of surface elemental composition, chemical state, positions, and relative area percentages of the deconvoluted C 1s, O 1s, and N 1s peaks obtained from the deconvolution of XPS spectra of all samples (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Marta E. Plonska-Brzezinska – Medical University of Białystok, Department of Organic Chemistry, Białystok 15-222, Poland; orcid.org/0000-0002-0538-6059; Email: marta.plonska-brzezinska@umb.edu.pl

Authors

Marcin Zajac – Medical University of Białystok, Department of Organic Chemistry, Białystok 15-222, Poland; orcid.org/0000-0002-8934-4218

Anthony Papathanassiou – National and Kapodistrian University of Athens, Physics Department, Zografos, Athens GR 15784, Greece; orcid.org/0000-0003-2744-4210

Kinga Ciecuch-Tymoniuk – Medical University of Białystok, Department of Organic Chemistry, Białystok 15-222, Poland; orcid.org/0009-0005-7885-289X

Krzysztof Brzezinski – Institute of Bioorganic Chemistry, Polish Academy of Sciences, Poznan 61-074, Poland; orcid.org/0000-0001-9339-7745

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsanm.5c05570>

Author Contributions

The manuscript was written through the contributions of all authors. All authors have given their approval to the final version of the manuscript.

Funding

Grant #2019/35/B/ST5/00572 (National Science Center, Poland, M.E.P.–B).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of the National Science Centre, Poland, grant #2019/35/B/ST5/00572 to M.E.P.–B. We gratefully acknowledge Prof. Luis Echegoyen from the University of Texas at El Paso for providing the CNOs. The

research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund (POIG.02.01.00-06024/09, Maria Curie-Skłodowska University, Poland).

■ REFERENCES

- (1) Jia, Y.; Jiang, K.; Wang, H.; Yao, X. The Role of Defect Sites in Nanomaterials for Electrocatalytic Energy Conversion. *Chem* **2019**, *5* (6), 1371–1397.
- (2) Chung, H. T.; Cullen, D. A.; Higgins, D.; Sneed, B. T.; Holby, E. F.; More, K. L.; Zelenay, P. Direct Atomic-Level Insight into the Active Sites of a High-Performance PGM-Free ORR Catalyst. *Science* **2017**, *357* (6350), 479–484.
- (3) Yan, D.; Li, Y.; Huo, J.; Chen, R.; Dai, L.; Wang, S. Defect Chemistry of Nonprecious-Metal Electrocatalysts for Oxygen Reactions. *Adv. Mater.* **2017**, *29* (48), 1606459.
- (4) Zhao, H.; Sun, C.; Jin, Z.; Wang, D.-W.; Yan, X.; Chen, Z.; Zhu, G.; Yao, X. Carbon for the Oxygen Reduction Reaction: A Defect Mechanism. *J. Mater. Chem. A* **2015**, *3* (22), 11736–11739.
- (5) Jiang, Y.; Yang, L.; Sun, T.; Zhao, J.; Lyu, Z.; Zhuo, O.; Wang, X.; Wu, Q.; Ma, J.; Hu, Z. Significant Contribution of Intrinsic Carbon Defects to Oxygen Reduction Activity. *ACS Catal.* **2015**, *5* (11), 6707–6712.
- (6) Tang, C.; Wang, H.-F.; Chen, X.; Li, B.-Q.; Hou, T.-Z.; Zhang, B.; Zhang, Q.; Titirici, M.-M.; Wei, F. Topological Defects in Metal-Free Nanocarbon for Oxygen Electrocatalysis. *Adv. Mater.* **2016**, *28* (32), 6845–6851.
- (7) He, Z.; Guo, Z.; Guo, K.; Akasaka, T.; Lu, X. Compositing Fullerene-Derived Porous Carbon Fibers with Reduced Graphene Oxide for Enhanced ORR Catalytic Performance. *C* **2022**, *8* (1), 13.
- (8) Liu, D.; Ni, K.; Ye, J.; Xie, J.; Zhu, Y.; Song, L. Carbon Nanomaterials: Tailoring the Structure of Carbon Nanomaterials toward High-End Energy Applications (Adv. Mater. 48/2018). *Adv. Mater.* **2018**, *30* (48), 1870371.
- (9) Zhu, J.; Huang, Y.; Mei, W.; Zhao, C.; Zhang, C.; Zhang, J.; Amiin, I. S.; Mu, S. Effects of Intrinsic Pentagon Defects on Electrochemical Reactivity of Carbon Nanomaterials. *Angew. Chem., Int. Ed.* **2019**, *58* (12), 3859–3864.
- (10) Gan, G.; Fan, S.; Li, X.; Wang, J.; Bai, C.; Guo, X.; Tade, M.; Liu, S. Nature of Intrinsic Defects in Carbon Materials for Electrochemical Dechlorination of 1,2-Dichloroethane to Ethylene. *ACS Catal.* **2021**, *11* (22), 14284–14292.
- (11) Zhu, J.; Mu, S. Defect Engineering in Carbon-Based Electrocatalysts: Insight into Intrinsic Carbon Defects. *Adv. Funct. Mater.* **2020**, *30* (25), 2001097.
- (12) Cao, Y.; Meng, Y.; Huang, S.; He, S.; Li, X.; Tong, S.; Wu, M.-N. Oxygen- and Sulfur-Doped Carbon-Encapsulated Ni₃S₂ and NiS Core–Shell Architectures: Bifunctional Electrocatalysts for Hydrogen Evolution and Oxygen Reduction Reactions. *ACS Sustainable Chem. Eng.* **2018**, *6* (11), 15582–15590.
- (13) Akhter, T.; Islam, M.; Faisal, S. N.; Haque, E.; Minett, A. I.; Liu, H. K.; Konstantinov, K.; Dou, S. X. Self-Assembled N/S Codoped Flexible Graphene Paper for High Performance Energy Storage and Oxygen Reduction Reaction. *ACS Appl. Mater. Interfaces* **2016**, *8* (3), 2078–2087.
- (14) Deng, L.; Fang, H.; Zhang, P.; Abdelkader, A.; Ren, X.; Li, Y.; Xie, N. Nitrogen and Sulfur Dual-Doped Carbon Microtubes with Enhanced Performances for Oxygen Reduction Reaction. *J. Electrochem. Soc.* **2016**, *163* (5), H343–H349.
- (15) Scardamaglia, M.; Susi, T.; Struzzi, C.; Snyders, R.; Di Santo, G.; Petaccia, L.; Bittencourt, C. Spectroscopic Observation of Oxygen Dissociation on Nitrogen-Doped Graphene. *Sci. Rep.* **2017**, *7* (1), 7960.
- (16) Hu, C.; Dai, L. Doping of Carbon Materials for Metal-Free Electrocatalysis. *Adv. Mater.* **2019**, *31* (7), 1804672.
- (17) Mbokazi, S. P.; Matthews, T.; Chabalala, M. P.; Selepe, C. T.; Mugadza, K.; Gwebu, S. S.; Mekuto, L.; Maxakato, N. W. Recent Progress on Carbon-Based Electrocatalysts for Oxygen Reduction Reaction: Insights on the Type of Synthesis Protocols, Performances

and Outlook Mechanisms. *ChemElectroChem* **2023**, *10* (21), No. e202300290.

(18) Cortie, M. B.; Supansomboon, S.; Dowd, A.; Arnold, M. D. Mesoporous Metal Sponges Produced by Explosive Decomposition. *ChemPhysChem* **2024**, *25* (19), No. e202400439.

(19) Song, H.; Guan, Z.; Chen, L.; Xu, H.; Xia, D.; Huang, M.; Li, D. Role of Curvature in a Carbon Electronic Structure under Spatial Confinement: Conversion of Nonradicals to Radicals. *Carbon* **2021**, *180*, 22–30.

(20) Wang, Y.; Bao, Z.; Shi, M.; Liang, Z.; Cao, R.; Zheng, H. The Role of Surface Curvature in Electrocatalysts. *Chem. – Eur. J.* **2022**, *28* (1), No. e202102915.

(21) Bates, K. R.; Scuseria, G. E. Why Are Buckyonions Round? *Theor. Chem. Acc.* **1998**, *99* (1), 29–33.

(22) Bagge-Hansen, M.; Bastea, S.; Hammons, J. A.; Nielsen, M. H.; Lauderbach, L. M.; Hodgins, R. L.; Pagoria, P.; May, C.; Aloni, S.; Jones, A.; et al. Detonation Synthesis of Carbon Nano-Onions via Liquid Carbon Condensation. *Nat. Commun.* **2019**, *10* (1), 3819.

(23) Mykhailiv, O.; Zubyk, H.; Brzezinski, K.; Gras, M.; Lota, G.; Gniadek, M.; Romero, E.; Echegoyen, L.; Plonska-Brzezinska, M. E. Improvement of the Structural and Chemical Properties of Carbon Nano-onions for Electrocatalysis. *ChemNanoMat* **2017**, *3* (8), 583–590.

(24) Mykhailiv, O.; Lapinski, A.; Molina-Ontoria, A.; Regulski, E.; Echegoyen, L.; Dubis, A. T.; Plonska-Brzezinska, M. E. Influence of the Synthetic Conditions on the Structural and Electrochemical Properties of Carbon Nano-Onions. *ChemPhysChem* **2015**, *16* (10), 2182–2191.

(25) Sang, S.; Yang, S.; Guo, A.; Gao, X.; Wang, Y.; Zhang, C.; Cui, F.; Yang, X. Hydrothermal Synthesis of Carbon Nano-Onions from Citric Acid. *Chem. – Asian J.* **2020**, *15* (21), 3428–3431.

(26) Wang, X.; Han, C.; Han, Y.; Huang, R.; Sun, H.; Guo, P.; Liu, X.; Huang, M.; Chen, Y.; Wu, H.; Zhang, J.; Yan, X.; Mao, Z.; Du, A.; Jia, Y.; Wang, L. Highly Curved Defect Sites: How Curvature Effect Influences Metal-Free Defective Carbon Electrocatalysts. *Small* **2024**, *20*, 2401447.

(27) Guo, K.; He, Z.; Lu, S.; Zhang, P.; Li, N.; Bao, L.; Yu, Z.; Song, L.; Lu, X. A Fullerene Seeded Strategy for Facile Construction of Nitrogen-Doped Carbon Nano-Onions as Robust Electrocatalysts. *Adv. Funct. Mater.* **2023**, *33* (29), 2302100.

(28) Kuznetsov, V. L.; Chuvilin, A. L.; Butenko, Y. V.; Mal'kov, I. Y.; Titov, V. M. Onion-like Carbon from Ultra-Disperse Diamond. *Chem. Phys. Lett.* **1994**, *222* (4), 343–348.

(29) Narayan, R. J.; Boehm, R. D.; Sumant, A. V. Medical Applications of Diamond Particles & Surfaces. *Mater. Today* **2011**, *14* (4), 154–163.

(30) Domonkos, M.; Ižák, T.; Stolicová, L.; Proška, J.; Demo, P.; Kromka, A. Structuring of diamond films using microsphere lithography. *Acta Polytech.* **2014**, *54* (5), 320–324.

(31) Kunuku, S.; Sankaran, K. J.; Tsai, C.-Y.; Chang, W.-H.; Tai, N.-H.; Leou, K.-C.; Lin, I.-N. Investigations on Diamond Nanostructuring of Different Morphologies by the Reactive-Ion Etching Process and Their Potential Applications. *ACS Appl. Mater. Interfaces* **2013**, *5* (15), 7439–7449.

(32) Tomita, S.; Burian, A.; Dore, J. C.; LeBolloch, D.; Fujii, M.; Hayashi, S. Diamond Nanoparticles to Carbon Onions Transformation: X-Ray Diffraction Studies. *Carbon* **2002**, *40* (9), 1469–1474.

(33) Siklitskaya, A. V.; Yastrebov, S. G.; Smith, R. An Interpretation of the Strongest X-Ray Diffraction Peak for Various Carbon Nanoclusters. *Nanosyst.: Phys., Chem., Math.* **2016**, *7*, 340–348.

(34) Liu, Y.; Vander Wal, R. L.; Khabashesku, V. N. Functionalization of Carbon Nano-Onions by Direct Fluorination. *Chem. Mater.* **2007**, *19* (4), 778–786.

(35) Antil, B.; Elkasabi, Y.; Strahan, G. D.; Vander Wal, R. L. Development of Graphitic and Non-Graphitic Carbons Using Different Grade Biopitch Sources. *Carbon* **2025**, *232*, 119770.

(36) Barinov, A.; Malcioğlu, O. B.; Fabris, S.; Sun, T.; Gregoratti, L.; Dalmiglio, M.; Kiskinova, M. Initial Stages of Oxidation on Graphitic Surfaces: Photoemission Study and Density Functional Theory Calculations. *J. Phys. Chem. C* **2009**, *113* (21), 9009–9013.

(37) Koinuma, M.; Tateishi, H.; Hatakeyama, K.; Miyamoto, S.; Ogata, C.; Funatsu, A.; Taniguchi, T.; Matsumoto, Y. Analysis of Reduced Graphene Oxides by X-Ray Photoelectron Spectroscopy and Electrochemical Capacitance. *Chem. Lett.* **2013**, *42* (8), 924–926.

(38) Arnault, J. C. X-Ray Photoemission Spectroscopy Applied to Nanodiamonds: From Surface Chemistry to in Situ Reactivity. *Diam. Relat. Mater.* **2018**, *84*, 157–168.

(39) Blume, R.; Rosenthal, D.; Tessonier, J.; Li, H.; Knop-Gericke, A.; Schlögl, R. Characterizing Graphitic Carbon with X-ray Photoelectron Spectroscopy: A Step-by-Step Approach. *ChemCatchem* **2015**, *7* (18), 2871–2881.

(40) Oh, Y. J.; Yoo, J. J.; Kim, Y. I.; Yoon, J. K.; Yoon, H. N.; Kim, J.-H.; Park, S. B. Oxygen Functional Groups and Electrochemical Capacitive Behavior of Incompletely Reduced Graphene Oxides as a Thin-Film Electrode of Supercapacitor. *Electrochim. Acta* **2014**, *116*, 118–128.

(41) Larciprete, R.; Lacovig, P.; Gardonio, S.; Baraldi, A.; Lizzit, S. Atomic Oxygen on Graphite: Chemical Characterization and Thermal Reduction. *J. Phys. Chem. C* **2012**, *116* (18), 9900–9908.

(42) Zhao, H.; Ye, J.; Song, W.; Zhao, D.; Kang, M.; Shen, H.; Li, Z. Insights into the Surface Oxygen Functional Group-Driven Fast and Stable Sodium Adsorption on Carbon. *ACS Appl. Mater. Interfaces* **2020**, *12* (6), 6991–7000.

(43) Tian, Z.; Dai, S.; Jiang, D. Stability and Core-Level Signature of Nitrogen Dopants in Carbonaceous Materials. *Chem. Mater.* **2015**, *27* (16), 5775–5781.

(44) Kiuchi, H.; Kondo, T.; Sakurai, M.; Guo, D.; Nakamura, J.; Niwa, H.; Miyawaki, J.; Kawai, M.; Oshima, M.; Harada, Y. Characterization of Nitrogen Species Incorporated into Graphite Using Low Energy Nitrogen Ion Sputtering. *Phys. Chem. Chem. Phys.* **2016**, *18* (1), 458–465.

(45) Celzard, A.; Collas, F.; Maréché, J. F.; Furdin, G.; Rey, I. Porous Electrodes-Based Double-Layer Supercapacitors: Pore Structure versus Series Resistance. *J. Power Sources* **2002**, *108* (1–2), 153–162.

(46) Simon, P.; Gogotsi, Y. Materials for Electrochemical Capacitors. *Nat. Mater.* **2008**, *7* (11), 845–854.

(47) Prabakaran, S. R. S.; Vimala, R.; Zainal, Z. Nanostructured Mesoporous Carbon as Electrodes for Supercapacitors. *J. Power Sources* **2006**, *161* (1), 730–736.

(48) Seyed Vahedein, Y.; Schrlau, M. G. Carbon Deposition Mechanisms Governing Template-Based Synthesis of Carbon Nanotubes. *Carbon* **2018**, *137*, 395–404.

(49) Balducci, A.; Belanger, D.; Brousse, T.; Long, J. W.; Sugimoto, W. Perspective—A Guideline for Reporting Performance Metrics with Electrochemical Capacitors: From Electrode Materials to Full Devices. *J. Electrochem. Soc.* **2017**, *164* (7), A1487–A1488.

(50) Barbieri, O.; Hahn, M.; Herzog, A.; Kötz, R. Capacitance Limits of High Surface Area Activated Carbons for Double Layer Capacitors. *Carbon* **2005**, *43* (6), 1303–1310.

(51) Pohlmann, S.; Lobato, B.; Centeno, T. A.; Balducci, A. The Influence of Pore Size and Surface Area of Activated Carbons on the Performance of Ionic Liquid Based Supercapacitors. *Phys. Chem. Chem. Phys.* **2013**, *15* (40), 17287.

(52) Connor, P.; Schuch, J.; Kaiser, B.; Jaegermann, W. The Determination of Electrochemical Active Surface Area and Specific Capacity Revisited for the System MnO_x as an Oxygen Evolution Catalyst. *Z. Für. Phys. Chem.* **2020**, *234* (5), 979–994.

(53) Schalenbach, M.; Selmert, V.; Kretzschmar, A.; Rajmakers, L.; Durmus, Y. E.; Tempel, H.; Eichel, R.-A. How Microstructures, Oxide Layers, and Charge Transfer Reactions Influence Double Layer Capacitances. Part I: Impedance Spectroscopy and Cyclic Voltammetry to Estimate Electrochemically Active Surface Areas (ECSAs). *Phys. Chem. Chem. Phys.* **2024**, *26* (19), 14288–14304.

(54) Li, R.; Li, H.; Long, J.; He, J.; Zhang, J.; Zheng, H.; Gou, X. Nitrogen and Phosphorus Dual-doped Porous Carbon Nanosheets for Efficient Oxygen Reduction in Both Alkaline and Acidic Media. *ChemCatchem* **2018**, *10* (18), 4038–4046.

(55) Mei, S.; Rui, X.; Li, L.; Huang, G.; Pan, X.; Ke, M.; Wang, Z.; Yu, H.; Yu, Y. Quantitative Coassembly for Precise Synthesis of

Mesoporous Nanospheres with Pore Structure-Dependent Catalytic Performance. *Adv. Mater.* **2021**, 33 (43), 2103130.

(56) Qiu, H.-J.; Chen, L. Y.; Ito, Y.; Kang, J. L.; Guo, X. W.; Liu, P.; Kashani, H.; Hirata, A.; Fujita, T.; Chen, M. W. An Ultrahigh Volumetric Capacitance of Squeezable Three-Dimensional Bicontinuous Nanoporous Graphene. *Nanoscale* **2016**, 8 (43), 18551–18557.

(57) Xiao, K.; Yang, T.; Liang, J.; Rawal, A.; Liu, H.; Fang, R.; Amal, R.; Xu, H.; Wang, D.-W. Nanofluidic Voidless Electrode for Electrochemical Capacitance Enhancement in Gel Electrolyte. *Nat. Commun.* **2021**, 12 (1), 5515.

(58) Seto, K.; Nakayama, T.; Uno, B. Formal Redox Potentials of Organic Molecules in Ionic Liquids on the Basis of Quaternary Nitrogen Cations as Adiabatic Electron Affinities. *J. Phys. Chem. B* **2013**, 117 (37), 10834–10845.

(59) Diallo, M. S.; Falconer, K.; Johnson, J. H.; Goddard, W. A. I. Dendritic Anion Hosts: Perchlorate Uptake by G5-NH₂ Poly-(Propyleneimine) Dendrimer in Water and Model Electrolyte Solutions. *Environ. Sci. Technol.* **2007**, 41 (18), 6521–6527.

(60) Liu, H.; Zhang, X.; Lv, Z.; Wei, F.; Liang, Q.; Qian, L.; Li, Z.; Chen, X.; Wu, W. Ternary Heterostructure Membranes with Two-Dimensional Tunable Channels for Highly Selective Ion Separation. *JACS Au* **2023**, 3 (11), 3089–3100.

(61) Deng, J.; Xue, G.; Li, C.; Zhao, S.; Zheng, Y.; He, Y.; Yuan, R.; Wang, K.; Mo, T.; Xiang, Y.; Chen, Y.; Geng, Y.; Wang, L.; Feng, G.; Hou, X.; Li, M. Accelerating Ion Desolvation via Bioinspired Ion Channel Design in Nonconcentrated Aqueous Electrolytes. *J. Am. Chem. Soc.* **2025**, 147 (7), 5943–5954.

(62) *Rotating Electrode Methods and Oxygen Reduction Electrocatalysts*; Elsevier, 2014. DOI: .

(63) Masa, J.; Batchelor-McAuley, C.; Schuhmann, W.; Compton, R. G. Koutecky-Levich Analysis Applied to Nanoparticle Modified Rotating Disk Electrodes: Electrocatalysis or Misinterpretation. *Nano Res.* **2014**, 7 (1), 71–78.

(64) Batchelor-McAuley, C.; Compton, R. G. Thin-Film Modified Rotating Disk Electrodes: Models of Electron-Transfer Kinetics for Passive and Electroactive Films. *J. Phys. Chem. C* **2014**, 118 (S1), 30034–30038.

(65) Soderberg, J. N.; Co, A. C.; Sirk, A. H. C.; Birss, V. I. Impact of Porous Electrode Properties on the Electrochemical Transfer Coefficient. *J. Phys. Chem. B* **2006**, 110 (21), 10401–10410.

(66) Wu, Z.; Yu, Y.; Zhang, G.; Zhang, Y.; Guo, R.; Li, L.; Zhao, Y.; Wang, Z.; Shen, Y.; Shao, G. In Situ Monitored (N, O)-Doping of Flexible Vertical Graphene Films with High-Flux Plasma Enhanced Chemical Vapor Deposition for Remarkable Metal-Free Redox Catalysis Essential to Alkaline Zinc–Air Batteries. *Adv. Sci.* **2022**, 9 (13), 2200614.

(67) Shin, D.; Jeong, B.; Choun, M.; Ocon, J. D.; Lee, J. Diagnosis of the Measurement Inconsistencies of Carbon-Based Electrocatalysts for the Oxygen Reduction Reaction in Alkaline Media. *RSC Adv.* **2015**, 5 (2), 1571–1580.

(68) Zhang, W.; Li, J.; Wei, Z. Carbon-Based Catalysts of the Oxygen Reduction Reaction: Mechanistic Understanding and Porous Structures. *Chin. J. Catal.* **2023**, 48, 15–31.

(69) Ma, R.; Lin, G.; Zhou, Y.; Liu, Q.; Zhang, T.; Shan, G.; Yang, M.; Wang, J. A Review of Oxygen Reduction Mechanisms for Metal-Free Carbon-Based Electrocatalysts. *Npj Comput. Mater.* **2019**, 5 (1), 78.

(70) Van Der Heijden, O.; Park, S.; Vos, R. E.; Eggebeen, J. J. J.; Koper, M. T. M. Tafel Slope Plot as a Tool to Analyze Electrocatalytic Reactions. *ACS Energy Lett.* **2024**, 9 (4), 1871–1879.

(71) Banham, D. W.; Soderberg, J. N.; Birss, V. I. Pt/Carbon Catalyst Layer Microstructural Effects on Measured and Predicted Tafel Slopes for the Oxygen Reduction Reaction. *J. Phys. Chem. C* **2009**, 113 (23), 10103–10111.

(72) Wang, Q.; Guesmi, H.; Tingry, S.; Cornu, D.; Holade, Y.; Minteer, S. D. Unveiling the Pitfalls of Comparing Oxygen Reduction Reaction Kinetic Data for Pd-Based Electrocatalysts without the Experimental Conditions of the Current–Potential Curves. *ACS Energy Lett.* **2022**, 7 (3), 952–957.

(73) Van Der Heijden, O.; Park, S.; Eggebeen, J. J. J.; Koper, M. T. M. Non-Kinetic Effects Convolute Activity and Tafel Analysis for the Alkaline Oxygen Evolution Reaction on NiFeOOH Electrocatalysts. *Angew. Chem., Int. Ed.* **2023**, 62 (7), No. e202216477.

(74) Blanc, N.; Rurainsky, C.; Tschulik, K. Implications of Resistance and Mass Transport Limitations on the Common Tafel Approach at Composite Catalyst Thin-Film Electrodes. *J. Electroanal. Chem.* **2020**, 872, 114345.

(75) Anantharaj, S.; Noda, S.; Driess, M.; Menezes, P. W. The Pitfalls of Using Potentiodynamic Polarization Curves for Tafel Analysis in Electrocatalytic Water Splitting. *ACS Energy Lett.* **2021**, 6, 1607–1611.

(76) Zhang, G.; Wei, Q.; Yang, X.; Tavares, A. C.; Sun, S. RRDE Experiments on Noble-Metal and Noble-Metal-Free Catalysts: Impact of Loading on the Activity and Selectivity of Oxygen Reduction Reaction in Alkaline Solution. *Appl. Catal., B* **2017**, 206, 115–126.

(77) Muhyuddin, M.; Mostoni, S.; Honig, H. C.; Mirizzi, L.; Elbaz, L.; Scotti, R.; D'Arienzo, M.; Santoro, C. Enhancing Electrocatalysis: Engineering the Fe–N_x–C Electrocatalyst for Oxygen Reduction Reaction Using Fe-Functionalized Silica Hard Templates. *ACS Appl. Energy Mater.* **2024**, 7 (24), 11691–11702.

(78) Ramaswamy, N.; Mukerjee, S. Fundamental Mechanistic Understanding of Electrocatalysis of Oxygen Reduction on Pt and Non-Pt Surfaces: Acid versus Alkaline Media. *Adv. Phys. Chem.* **2012**, 2012, 1–17.

(79) Wang, H.; Xu, Z.; Kohandehghan, A.; Li, Z.; Cui, K.; Tan, X.; Stephenson, T. J.; King'ondo, C. K.; Holt, C. M. B.; Olsen, B. C.; Tak, J. K.; Harfield, D.; Anyia, A. O.; Mitlin, D. Interconnected Carbon Nanosheets Derived from Hemp for Ultrafast Supercapacitors with High Energy. *ACS Nano* **2013**, 7 (6), 5131–5141.

(80) Garsany, Y.; Baturina, O. A.; Swider-Lyons, K. E.; Kocha, S. S. Experimental Methods for Quantifying the Activity of Platinum Electrocatalysts for the Oxygen Reduction Reaction. *Anal. Chem.* **2010**, 82 (15), 6321–6328.

(81) Zhang, D.; Wang, Z.; Liu, F.; Yi, P.; Peng, L.; Chen, Y.; Wei, L.; Li, H. Unraveling the pH-Dependent Oxygen Reduction Performance on Single-Atom Catalysts: From Single- to Dual-Sabatie Optima. *J. Am. Chem. Soc.* **2024**, 146 (5), 3210–3219.

(82) Liu, H. J.; Chan, C. T.; Liu, Z. Y.; Shi, J. Density Functional Study of Oxygen Adsorption on 4-Å Carbon Nanotubes. *Phys. Rev. B* **2005**, 72 (7), 075437.

(83) Giannozzi, P.; Car, R.; Scoles, G. Oxygen Adsorption on Graphite and Nanotubes. *J. Chem. Phys.* **2003**, 118 (3), 1003–1006.

(84) Dumitrică, T.; Landis, C. M.; Jakobson, B. I. Curvature-Induced Polarization in Carbon Nanoshells. *Chem. Phys. Lett.* **2002**, 360 (1–2), 182–188.

(85) Sabalot-Cuzzubbo, J.; Salvato-Vallverdu, G.; Bégue, D.; Cresson, J. Relating the Molecular Topology and Local Geometry: Haddon's Pyramidalization Angle and the Gaussian Curvature. *J. Chem. Phys.* **2020**, 152 (24), 244310.

(86) Wen, H.; Zhao, Z.; Luo, Z.; Wang, C. Unraveling the Impact of Curvature on Electrocatalytic Performance of Carbon Materials: A State-of-the-Art Review. *ChemSuschem* **2024**, 17 (10), No. e202301859.