



Upcycled polymer waste-derived N-doped carbon supports enabling durable PtCo catalysts for PEM fuel cells

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ABSTRACT

Upcycling plastic waste into functional electrocatalyst supports enables a sustainable pathway for advancing fuel cell technologies. Herein, we develop nitrogen-doped carbon supports via a one-pot Friedel-Crafts reaction between waste polystyrene and pyrrole, enabling simultaneous hyper-crosslinking and nitrogen (N) incorporation without post-treatment. Upon carbonization, the resulting framework exhibits tunable N content and hierarchical porosity, providing a robust platform for proton exchange membrane fuel cell catalysts. N doping regulates ionomer distribution and strengthens Co–N coordination, promoting the formation of uniformly dispersed intermetallic PtCo nanoparticles with enhanced structural stability. Density functional theory calculations reveal that subsurface Co induces a downshift of the Pt d-band center, weakening *O adsorption and accelerating oxygen reduction reaction kinetics. As a result, the catalysts deliver a mass activity of 0.84 A mg_{Pt}^{−1} at 0.9 V, approaching twice the U.S. DOE 2025 target. In full-cell tests, a peak power density of 1180 mW cm^{−2} is achieved and retained at 1024 mW cm^{−2} after 30,000 potential cycles, demonstrating excellent durability. This work presents a scalable and cost-effective strategy that integrates plastic waste upcycling with rational catalyst design, offering a viable route toward high-performance PEMFC systems.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are among the most promising electrochemical energy conversion technologies for hydrogen-powered transportation and stationary power systems [1–3]. However, their widespread adoption is impeded by the intrinsically sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode, the reliance on scarce and expensive platinum (Pt)-based catalysts, and insufficient long-term durability [4–6]. In particular, the cathode

catalyst layer remains a critical bottleneck, where limited ORR activity, inefficient oxygen transport, poor proton conduction, and structural degradation of carbon supports collectively restrict overall performance [7,8]. While advances in catalyst nanostructuring have enabled mass activities surpassing the U.S. Department of Energy (DOE) target (0.44 A mg_{Pt}^{−1} at 0.9 V), these systems often fail to maintain performance under operating conditions due to Pt dissolution, nanoparticle agglomeration, and carbon support corrosion [9–11]. Therefore, developing catalyst architectures that simultaneously enhance activity and durability under

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practical operating conditions remains a critical challenge for PEMFC commercialization [12].

Heteroatom doping of carbon materials, particularly nitrogen (N) doping, has been widely explored as an effective strategy to enhance ORR catalyst performance by improving metal nanoparticle anchoring and regulating ionomer distribution within catalyst layers [13–21]. For example, Ott et al. demonstrated that N-doped carbon surfaces enable homogeneous ionomer dispersion through electrostatic interactions, thereby enhancing proton conductivity and catalyst utilization in membrane electrode assemblies (MEAs) [22]. Gong et al. further reported that amino-functionalized carbon supports guide the selective deposition of PtCo nanoparticles onto mesoporous external surfaces, minimizing micropore blockage and reducing mass transport resistance [23]. Despite these advantages, conventional doping approaches, including ammonia annealing, plasma treatment, and precursor blending, often suffer from limited scalability, low carbon yield, and insufficient control over doping levels [24–28]. Therefore, developing scalable synthetic strategies that enable efficient N incorporation while maintaining structural integrity remains essential for the practical production of high-performance N-doped carbon supports for PEMFC applications.

A promising strategy for synthesizing N-doped porous carbons involves the Friedel–Crafts reaction, which has been widely employed to construct hyper-crosslinked polymer networks from aromatic monomers [29–31]. This reaction proceeds under relatively mild conditions and accommodates a wide range of N-containing precursors, including heterocyclic compounds such as pyridine and pyrrole, enabling efficient incorporation of N functionalities [32–35]. Importantly, the Friedel–Crafts reaction is also compatible with polystyrene (PS), an abundant plastic waste composed of aromatic repeating units [36–39]. The aromatic structure of PS makes it a suitable carbon precursor for constructing porous carbon frameworks through hyper-crosslinking and carbonization. Utilizing waste PS as a carbon source not only provides a sustainable route for plastic waste valorization but also enables scalable synthesis of N-rich carbon frameworks through a cost-effective upcycling process. Despite increasing interest in plastic-derived carbons, most reported systems lack precise control over interfacial properties, particularly carbon–ionomer interactions that critically govern catalyst layer performance under practical operating conditions. Therefore, scalable strategies that enable simultaneous control of composition, porosity, and interfacial characteristics are urgently needed.

Herein, we report the development of N-doped carbon supports derived from upcycled PS (NPS) for high-performance and durable PEMFC electrocatalysts. A solvent-assisted Friedel–Crafts hyper-crosslinking strategy using pyrrole enables the formation of N-rich polymer networks with precisely tunable compositions, which are subsequently converted into N-doped carbon frameworks through carbonization. The resulting carbon supports provide abundant N functionalities that promote strong metal–support interactions and stabilize intermetallic PtCo nanoparticles via Co–N coordination. In addition to stabilizing the catalyst structure, the N-doped surface modulates carbon–ionomer interactions, leading to improved ionomer dispersion and optimized triple-phase boundary formation within the catalyst layer. As a result, the PtCo catalysts supported on the N-doped carbons (PtCo/NPS) exhibit enhanced ORR activity and remarkable durability in both half-cell and membrane electrode assembly (MEA) tests, delivering a mass activity of $0.84 \text{ A mg}_{\text{Pt}}^{-1}$ at 0.9 V and a peak power density of 1180 mW cm^{-2} , with the latter retaining 86.8% of its initial value after 30,000 cycles. This work demonstrates a scalable and economically viable strategy for transforming plastic waste into functional catalyst supports while simultaneously improving catalyst utilization and durability in practical PEMFC systems.

2. Experimental section

2.1. Materials

Waste PS was collected from packaging materials used for chemical bottles. Formaldehyde dimethyl acetal (FDA, 99%), iron (III) chloride (FeCl_3 , 97%), pyrrole (98%), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\geq 37.5\%$ Pt) and cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 97%) were purchased from Sigma-Aldrich. 1,2-Dichloroethane (DCE, 99%), methanol (99.5%), acetone (99.5%), ethanol (99%) and isopropanol (IPA, 99.5%) were supplied by Daejung. Commercial Pt/C (20 wt%, Tanaka Kikinzoku Kogyo, TEC10E20E), and Nafion 212 membrane (50 μm , DuPont) and all reagents were used as received, without further purification.

2.2. Synthesis of NPS

1 g of waste PS and 1 g of FeCl_3 were mixed in 100 mL of DCE. After the reactants were uniformly dispersed in the solution, pyrrole was added in varying amounts to control the N doping level. Subsequently, 1 mL of FDA was added dropwise, and the reaction mixture was stirred at 80 °C for 24 h. The resulting product was washed with methanol to remove FeCl_3 and dried overnight in a vacuum oven at 60 °C. Here, FeCl_3 served only as a Lewis acid catalyst for the Friedel–Crafts cross-linking reaction, and other Lewis acid salts such as AlCl_3 could also be employed. Residual Fe species were effectively removed by the washing process [40]. The obtained polymer precursor was then carbonized at 950 °C for 1.5 h under a N_2 atmosphere to produce NPS. The resulting samples were denoted as NPS0, NPS1, NPS2, and NPS3, corresponding to pyrrole-to-styrene repeat unit molar ratios of 0, 1/8, 1/4, and 1/2, respectively.

2.3. Synthesis of PtCo/NPS catalysts

$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (114 mg) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (101 mg) were dissolved in acetone (50 mL) and mixed with the NPS support (100 mg). The suspension was sonicated until the precursors were uniformly dispersed. The solvent was subsequently removed by evaporation in a vacuum oven. The obtained mixture was then pyrolyzed at 600 °C for 2 h under a reducing atmosphere ($\text{H}_2/\text{Ar} = 100/900 \text{ sccm}$) with a ramp rate of $10^\circ\text{C min}^{-1}$ to form PtCo intermetallic nanoparticles, yielding the PtCo/NPS catalysts. The ordering degree was calculated using the following equation: [41].

$$\text{ordering degree (\%)} = \frac{S_{110}/S_{111}}{I_{110}^0/I_{111}^0} \times 100$$

Here, S_{110} and S_{111} represent the integrated peak areas of the (110) superlattice and (111) fundamental reflections, respectively, obtained from the XRD patterns. I_{110} and I_{111} denote the corresponding peak intensities of the (110) and (111) reflections obtained from the PtCo reference pattern (#96–152–5473).

2.4. Characterization

Morphological and structural properties of the carbon supports were characterized using scanning electron microscopy (SEM, Nova Nano SEM 450) and Raman spectroscopy (Horiba LabRam GR UV/Vis/NIR). The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were determined using a surface area and pore size analyzer (Quantachrome Autosorb IQ). The chemical compositions of NPS and PtCo/NPS were analyzed using an elemental analyzer (EA, Ckic 5E-CHN2200), X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-Alpha), X-ray diffraction (XRD, Rigaku SmartLab 9 kW), and inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Fisher Scientific iCAP7600). X-ray absorption near-edge

structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were conducted at the Pohang Light Source (PLS) 8C Nano XAFS beamline. The morphology and composition of PtCo/NPS were further investigated using transmission electron microscopy (TEM, Titan G2 Cube 60–300) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Thermo Fisher Scientific Spectra Ultra).

2.5. Electrochemical characterization

Half-cell electrochemical measurements were performed using a three-electrode system equipped with a CHI760E potentiostat and a rotating ring-disk electrode (RRDE). All potentials were initially measured against an Ag/AgCl reference electrode and converted to the reversible hydrogen electrode (RHE) scale. Catalyst ink was prepared by dispersing 5 mg of catalyst in a mixed solution containing 20 μL of Nafion solution, 0.5 mL of deionized water, and 2 mL of IPA, followed by ultrasonication for 1 h to ensure homogeneous dispersion. 15 μL of ink was drop-cast onto a glassy carbon electrode. Cyclic voltammetry (CV) measurements were conducted in Ar-saturated 0.1 M HClO_4 electrolyte at a scan rate of 100 mV s^{-1} . ORR activity was evaluated using linear sweep voltammetry (LSV) in O_2 -saturated 0.1 M HClO_4 at a scan rate of 10 mV s^{-1} with a rotation speed of 1600 rpm. Accelerated durability tests were performed by cycling the potential between 0.6 and 1.0 V_{RHE} for 10,000 cycles in an Ar-saturated electrolyte.

Single-cell performance was evaluated using a PEM fuel cell testing system (SMART2, WonATech). The electrodes were prepared using the catalyst-coated substrate (CCS) method by spray-coating catalyst ink onto a gas diffusion layer (GDL) with an active area of 5 cm^2 . The catalyst ink consisted of 30 mg catalyst powder, 1 mL deionized water, 3 mL IPA, and 5 wt% Nafion solution to achieve an ionomer-to-carbon (I/C) ratio of 0.8. A Nafion 212 membrane was used as the polymer electrolyte membrane and assembled between the anode and cathode at elevated temperature to form the MEA. The fuel cell was operated at 80 $^\circ\text{C}$ and 100% relative humidity (RH). H_2 and O_2 were supplied at flow rates of 300 and 600 sccm, respectively, with a backpressure of 1.5 bar.

Catalyst durability was further evaluated using an accelerated stress test (AST) based on the DOE protocol. The AST was performed for 30,000 potential cycles between 0.6 and 0.95 V, with a holding time of 3 s at each potential. During the test, N_2 (75 sccm) was supplied to the cathode, while humidified H_2 (200 sccm) was fed to the anode.

2.6. Computational method

All DFT calculations were performed using the Vienna ab initio simulation package (VASP, version 5.4.4) [42,43]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was used to account for exchange-correlation effects, and the projector augmented-wave (PAW) method was applied [44–46]. The surfaces were modeled using a 4×4 supercell with four atomic layers and 15 $\text{\AA}$ vacuum in the z-direction to eliminate image–image interactions under periodic boundary conditions. For all the surface calculations, we fixed the bottom two layers of the slab, while the top two layers and the adsorbates were allowed to relax. The plane-wave cutoff used for all the geometry optimizations was set to 550 eV [47]. The Brillouin zone was sampled using a Γ -centered k-point mesh: $9 \times 9 \times 9$ for Pt bulk, $7 \times 7 \times 7$ for PtCo bulk, and $3 \times 3 \times 1$ for all slab models and adsorption models. The thresholds for force and energy convergence were set to 0.02 eV/ $\text{\AA}$ and 10^{-6} eV.

The adsorption energy of every adsorbate on the catalyst surface, represented as ΔE , is defined as follows:

$$\Delta E = E_{\text{adsorbate}^+} - (E_{\text{adsorbate(gas)}} + E^*) \quad (1)$$

Where * denotes the catalyst surface, and E^* , $E_{\text{adsorbate(gas)}}$ and $E_{\text{adsorbate}^+}$ represent the energies for a bare catalyst surface, an

adsorbate molecule in the gas phase, and an adsorbed catalyst surface, respectively.

Free energies of the ORR intermediates in electrochemical reaction pathways were calculated based on the computational hydrogen electrode (CHE) model proposed by Nørskov et al. [48]. The CHE model suggests that the chemical potential of a proton/electron ($\text{H}^+ + \text{e}^-$) is equal to half of the chemical potential of a gas-phase H_2 molecule. Free energy changes (ΔG) of all ORR steps on the catalyst surface were determined as follows.

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S + \Delta G_{\text{pH}}, \quad (2)$$

ΔE is the total energy change obtained from DFT calculation, ΔZPE and ΔS are the zero-point energy difference and the entropy difference between the adsorbed state and the gas phase, respectively, and T is the system temperature (353.15 K in this work). ΔG_{pH} is the free energy contribution due to variations in H^+ concentration, and in this work the value of pH was assumed to be 1 for 0.1 M HClO_4 medium.

3. Results and discussion

3.1. Synthesis of NPS

A one-pot scalable strategy was developed to synthesize N-doped carbon materials via a Friedel–Crafts alkylation reaction. As illustrated in Fig. 1, this approach enables simultaneous hyper-crosslinking of PS and incorporation of N functionalities into the resulting carbon framework through a Friedel–Crafts reaction between PS and pyrrole. To demonstrate the concept of plastic upcycling, waste PS collected from chemical bottle packaging was used as the primary carbon source (Fig. S1). During synthesis, waste PS, FeCl_3 , pyrrole, and FDA were dissolved in DCE. The Friedel–Crafts reaction between styrene units in PS and pyrrole enabled concurrent network formation and N incorporation in a single step. To systematically tune the N content, pyrrole was introduced at molar ratios of 0, 1/8, 1/4, and 1/2 relative to the styrene units, yielding samples denoted as NPS0, NPS1, NPS2, and NPS3, respectively. After filtration and solvent removal, the crosslinked polymers were carbonized at 950 $^\circ\text{C}$ under N_2 to produce the corresponding NPS materials. To investigate the influence of N doping on catalytic performance, PtCo intermetallic nanoparticles were deposited onto NPS0 and NPS3 using a wet impregnation method. Pt and Co precursors were co-dissolved in acetone, impregnated onto the carbon supports, and subsequently thermally treated at 600 $^\circ\text{C}$ under H_2/Ar to yield alloy catalysts denoted as PtCo/NPS0 and PtCo/NPS3.

Thermogravimetric analysis (TGA) highlights the critical role of hyper-crosslinking in improving carbonization yield (Fig. S2). Pristine waste PS exhibited a low residual yield of 4.38%, whereas hyper-crosslinked NPS0 showed a substantially higher residual yield of 30.81%, demonstrating that the Friedel–Crafts reaction improves the thermal stability and carbonization behavior of the PS precursor. The residual yield further increased to 40.6% for NPS3 after pyrrole incorporation, indicating that pyrrole contributes significantly to the carbon yield. Consistently, a polypyrrole control sample exhibited a relatively high residual yield of 45.9%. However, the thermal decomposition profile of NPS3 was distinct from that of polypyrrole, with NPS3 maintaining a high weight fraction up to approximately 400 $^\circ\text{C}$ before undergoing a distinct decomposition step. These results indicate that pyrrole contributes to the increased carbon yield, while the Friedel–Crafts-derived network governs the distinct thermal decomposition behavior of NPS3. This network formation facilitates the development of graphitic domains and enables uniform N incorporation throughout the carbon matrix.

Pristine waste PS exhibits a macroporous morphology with pore sizes exceeding $\sim 100 \mu\text{m}$, likely originating from residual foaming agents used during manufacturing (Fig. S3a). The waste PS readily dissolves in the reaction solvent (e.g., DCE), as shown in Fig. S3b. During the reaction, in situ crosslinking induces collapse of the original porous

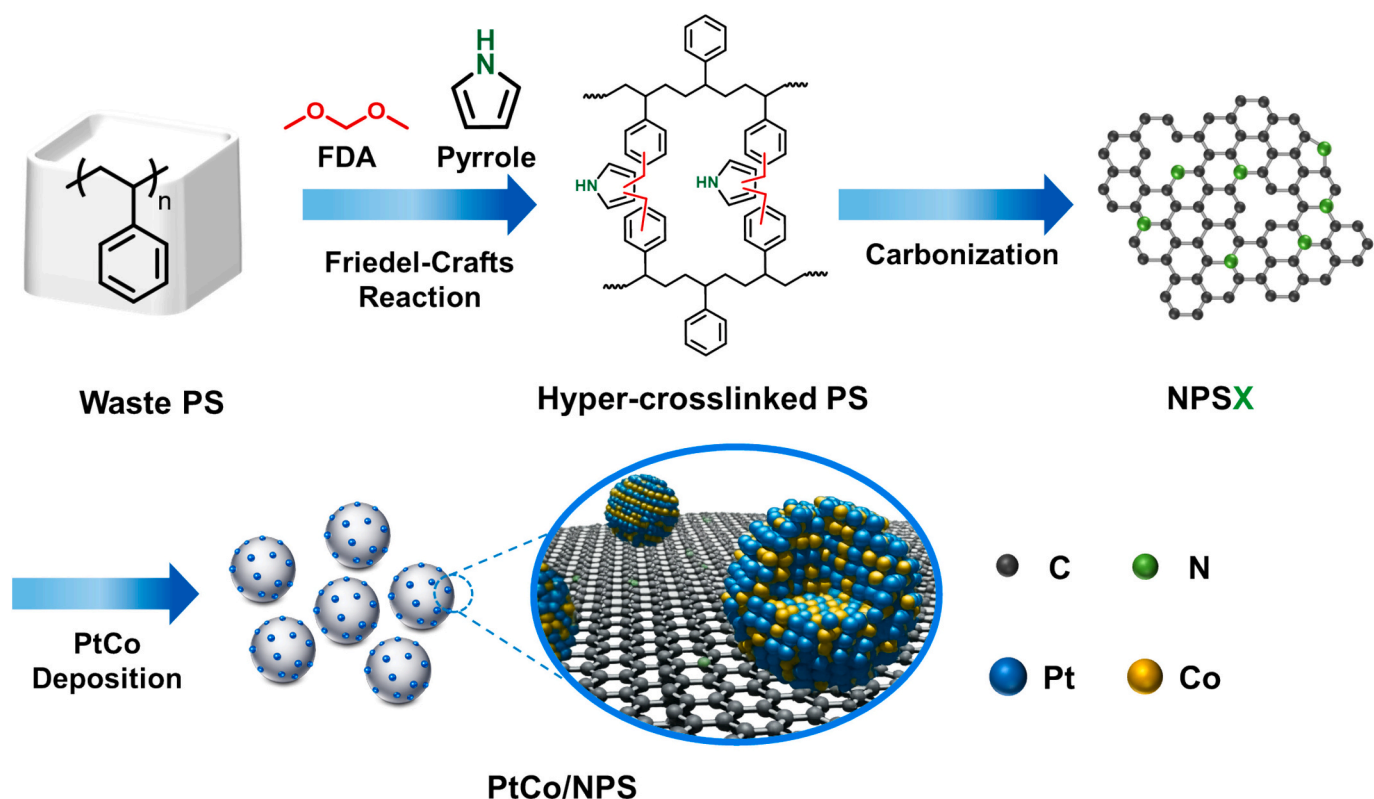


Fig. 1. Schematic illustration of the one-pot synthesis of NPS from waste polystyrene via pyrrole-assisted Friedel-Crafts hyper-crosslinking and the subsequent formation of PtCo/NPS catalysts.

structure, leading to the formation of crosslinked polymer domains. The inclusion of pyrrole significantly influences this morphological evolution, yielding an increasing number of smaller spherical domains with higher pyrrole content, as confirmed by SEM (Fig. S4). After carbonization, the hyper-crosslinked nanostructure is well retained across the

NPS series, producing carbon materials composed of uniformly dispersed nanoscale domains with diameters of approximately 50–60 nm (Fig. 2a–d). This result indicates that the polymer-derived architecture effectively serves as a morphological template for generating finely structured carbon frameworks. To verify whether the N content in

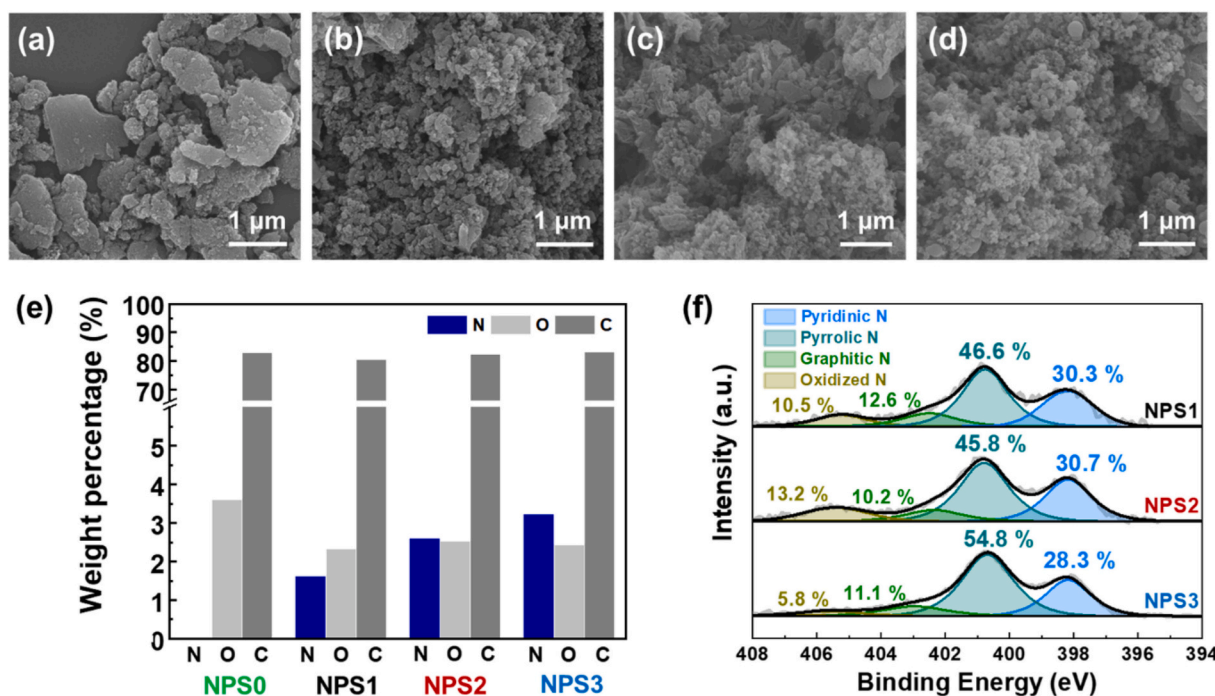


Fig. 2. SEM images of (a) NPS0, (b) NPS1, (c) NPS2, and (d) NPS3. (e) EA results showing the weight composition of C, N, and O in the NPS samples. (f) High-resolution XPS N 1s spectra of NPS1, NPS2, and NPS3 with deconvolution into different N species.

the carbon framework could be modulated by the amount of pyrrole, elemental analysis (EA) was performed. The N content in NPS1, NPS2, and NPS3 gradually increased to 1.62%, 2.61%, and 3.24%, respectively, demonstrating that pyrrole acts as an effective N source during the crosslinking and carbonization processes (Fig. 2e, Table S1). In addition, the waste PS exhibited a high carbon content, while trace amounts of N, O, and S were detected, which may originate from minor additives or surface contaminants associated with commercial packaging foam. S was no longer detected in the resulting NPS samples, indicating that S-containing impurities were effectively removed during the synthetic process. To examine the attainable N content, NPS4 and NPS5 were prepared at higher PS:pyrrole molar ratios of 1:1.0 and 1:1.33, respectively. EA showed N contents of 3.59% for NPS4 and 3.03% for NPS5, indicating that the N content attainable under the present synthesis conditions is approximately 3–4 wt%.

XRD analysis of the pristine NPS supports revealed a broad carbon (002) diffraction feature, suggesting the formation of a turbostratic carbon framework (Fig. S5a). XPS was employed to investigate the chemical bonding environments of N and carbon species in the NPS samples. The surface atomic concentration of N, determined from the survey spectra, increased from 1.42% in NPS1 to 2.15% in NPS2 and 5.09% in NPS3, consistent with the EA results (Fig. S5b, Table S2). High-resolution N 1 s and C 1 s spectra provided further insight into the bonding configurations within the carbon framework. The N 1 s spectra were deconvoluted into four components corresponding to pyridinic N (~398 eV), pyrrolic N (~400 eV), graphitic N (~401–402 eV), and oxidized N (~405 eV) (Fig. 2f) [49]. Among these, pyrrolic N was the dominant species (~50%), followed by pyridinic N (~30%), graphitic N (~11%), and oxidized N (~10%). These N functionalities are known to modulate the electronic structure of carbon materials and facilitate electron transfer during electrocatalytic reactions [50,51]. In addition, the presence of N functionalities may promote improved ionomer distribution on the catalyst surface, which can enhance catalyst–electrolyte interfacial interactions relevant to fuel cell performance [52]. The high-

resolution C 1 s spectra were deconvoluted into five components corresponding to C–C (sp^2 , 284.5 eV), C–C (sp^3 , 285.4 eV), C–N (286.2 eV), C–O (287.0 eV), and C=O (288.8 eV) (Fig. S6). Notably, the C–N bonding contribution increased with pyrrole content, from 4.82% (NPS1) to 5.77% (NPS2) and 6.69% (NPS3), confirming successful N incorporation into the carbon framework [53]. Furthermore, the absence of detectable Fe signals in the XPS survey spectra confirms that residual Fe species from the Friedel–Crafts reaction were effectively removed during the washing process.

Raman spectroscopy provided complementary insights into the carbon structure (Fig. S7). All samples exhibited characteristic D and G bands at ~1350 and ~1580 cm^{-1} , respectively, corresponding to disordered and graphitic carbon structures [54]. The I_D/I_G ratio gradually increased from 1.02 for NPS0 to 1.21 for NPS3, suggesting that N incorporation introduces additional structural defects into the carbon lattice. N_2 adsorption–desorption isotherms revealed distinct evolution of the pore structure (Fig. S8). While NPS0 displayed a type I isotherm characteristic of microporous materials, NPS1–NPS3 exhibited H3-type hysteresis loops indicative of mesopore formation [55,56]. The BET surface area increased with N incorporation, from 31.95 $m^2 g^{-1}$ for NPS1 to 115.61 $m^2 g^{-1}$ for NPS3 (Table S3).

3.2. Characterization of PtCo/NPS catalysts

To systematically investigate the role of N-doping in metal–support interactions, PtCo catalysts were supported on N-free (NPS0) and N-rich (NPS3) carbon frameworks. XRD analysis confirmed the formation of an ordered PtCo intermetallic phase (Fig. 3a). The characteristic (111), (200), and (220) diffraction peaks appeared at higher angles (41.0°, 47.6°, and 69.9°), indicating lattice contraction resulting from Co incorporation into the Pt lattice [57,58]. Notably, PtCo/NPS3 exhibited a more discernible (110) superlattice reflection together with clearer splitting of the (200)/(002) diffraction peaks at around 47–49° than PtCo/NPS0, suggesting a higher degree of ordered intermetallic PtCo

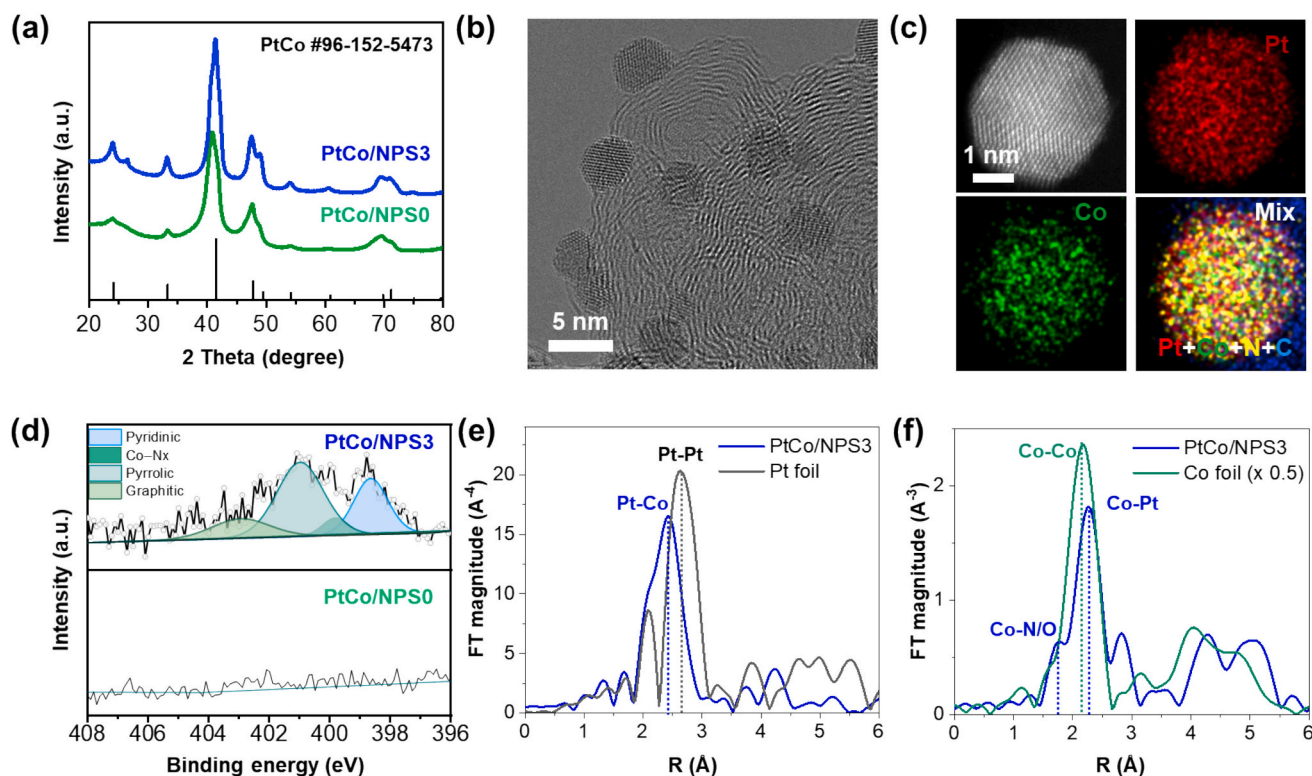


Fig. 3. (a) XRD patterns of PtCo/NPS3 and PtCo/NPS0. (b) STEM images of PtCo/NPS catalysts. (c) High-resolution STEM image and corresponding EDS elemental mapping of PtCo/NPS3. (d) High-resolution N 1 s XPS spectra of PtCo/NPS3 and PtCo/NPS0. (e) Pt L_{3} -edge and (f) Co K-edge EXAFS spectra of PtCo/NPS3.

formation on the N-rich support. Such ordered intermetallic structures are known to enhance structural stability and modulate the Pt electronic structure, thereby optimizing ORR intermediate adsorption [59,60]. The ordering degree was further estimated from the integrated intensity ratio of the (110) superlattice peak to the (111) fundamental peak using the PtCo reference pattern. The ordering degrees of PtCo/NPS0 and PtCo/NPS3 were approximately 11% and 25%, respectively. ICP-OES analysis confirmed that the Pt loading was consistently around 30 wt% across all samples (Table S4). TEM images suggest that PtCo nanoparticles are uniformly dispersed on both NPS0 and NPS3 supports (Fig. 3b, Fig. S9a–b). This uniform dispersion, despite the moderate BET surface area of NPS3, is attributed to the N-containing and defect-rich carbon surface, which provides preferential anchoring sites for Pt/Co precursors and promotes more homogeneous nucleation during catalyst synthesis [61,62]. The average particle sizes of PtCo/NPS0 and PtCo/NPS3 were 5.33 ± 1.75 nm and 4.28 ± 1.10 nm, respectively (Fig. S9c–d). High-resolution STEM images revealed clear lattice fringes characteristic of the ordered PtCo intermetallic structure (Fig. S10a–b). EDS mapping showed uniform distribution of C, N, Pt, and Co across the catalyst surface, suggesting possible interactions between N functionalities and PtCo nanoparticles (Fig. 3c). This observation is further supported by line profile analysis showing a Pt-enriched outer layer surrounding the Co-containing core, consistent with the formation of a Pt-skin intermetallic structure (Fig. S10c).

XPS was performed to investigate the surface chemical states of the catalysts. Both catalysts exhibit characteristic peaks corresponding to C 1s, O 1s, Co 2p, and Pt 4f, whereas the N 1s signal is observed only for PtCo/NPS3 (Fig. S11). The high-resolution N 1s spectrum of PtCo/NPS3 was deconvoluted into five components corresponding to pyridinic N (~ 399.0 eV), Co–N_x (~ 399.8 eV), pyrrolic N (~ 401.0 eV), graphitic N (~ 402.0 eV), and oxidized N (~ 403 – 405 eV) (Fig. 3d) [63,64]. The presence of the Co–N_x component suggests possible coordination between N functionalities and Co atoms, indicating enhanced metal–support interactions induced by N-doping [65]. In contrast, the corresponding spectrum of PtCo/NPS0 prepared on N-free carbon exhibits no detectable N 1s signal, confirming the absence of N functionalities. The Pt 4f spectrum reveals a significantly higher fraction of metallic Pt⁰ (74.3%) in PtCo/NPS3 compared to commercial Pt/C (51.9%), indicating that Pt exists in a more reduced state (Fig. S11b). A similar Pt⁰ fraction is observed for PtCo/NPS0, indicating that the reduced Pt state primarily originates from alloying with Co.

XANES and EXAFS measurements were performed to further probe the local coordination environment and electronic structure of PtCo/NPS3. The Pt L₃-edge XANES spectrum of PtCo/NPS3 shows a profile similar to that of Pt foil, indicating that Pt predominantly exists in a metallic state within the intermetallic phase (Fig. S12a) [66,67]. This observation is consistent with the high Pt⁰ fraction identified in the Pt 4f XPS spectrum. In contrast, the Co K-edge XANES spectrum exhibits an edge position close to that of Co foil but with a slightly higher white-line intensity, suggesting the presence of partially oxidized Co species in addition to metallic Co (Fig. S12b). The k³-weighted Fourier-transformed EXAFS spectra at the Pt L₃-edge display a dominant peak at a shorter radial distance compared with Pt foil, which can be assigned to Pt–Co coordination (Fig. 3e) [68,69]. This feature confirms the formation of an ordered Pt–Co intermetallic structure. At the Co K-edge, the dominant coordination is attributed to Co–Pt interactions, while no obvious Co–Co feature is observed, further confirming the alloyed nature of the catalyst structure (Fig. 3f). Notably, an additional peak at lower radial distance may originate from Co–N/O coordination, consistent with the Co–N_x component observed in the N 1s XPS spectrum. This result suggests strong interactions between Co species and N functionalities in the doped carbon support, which can serve as effective anchoring sites for the alloy nanoparticles [70,71].

3.3. Electrochemical characterization

The ORR activities of the NPS-supported catalysts were systematically investigated using a standard three-electrode half-cell rotating ring-disk electrode (RRDE) setup. For comparison, commercial Pt/C (20 wt% Pt) was also evaluated under the same conditions. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) curves were obtained in 0.1 M HClO₄ solution, yielding mass activities of 0.20, 0.42, and 1.03 A mg_{Pt}^{−1} at 0.9 V_{RHE} with iR compensation for commercial Pt/C, PtCo/NPS0, and PtCo/NPS3, respectively (Fig. S13, Fig. S14a). All NPS-supported catalysts outperformed commercial Pt/C, highlighting the beneficial effect of Co alloying on ORR activity. The electrochemical surface area (ECSA) was determined from the hydrogen underpotential deposition (HUPD) region by averaging the integrated areas of hydrogen adsorption and desorption. The initial ECSA values were calculated to be 63.2, 40.8, and 62.8 m² g_{Pt}^{−1} for commercial Pt/C, PtCo/NPS0, and PtCo/NPS3, respectively. Accelerated durability tests (ADT) were conducted by potential cycling between 0.6 and 1.0 V at a scan rate of 100 mV s^{−1} for 10,000 cycles. After 10,000 cycles, PtCo/NPS3 retained a high mass activity of 0.95 A mg_{Pt}^{−1} at 0.9 V_{RHE}, significantly outperforming PtCo/NPS0 (0.28 A mg_{Pt}^{−1}) and commercial Pt/C (0.09 A mg_{Pt}^{−1}) (Fig. S14b). The enhanced durability is ascribed to strong Co–N interactions that anchor the intermetallic structure, as revealed by X-ray analysis, thereby suppressing metal dissolution and structural degradation. A similar trend was observed in the ECSA retention after durability testing. PtCo/NPS3 preserved 84.9% of its initial ECSA, while PtCo/NPS0 and Pt/C retained 63.2% and 66.6% respectively (Fig. S14c).

To elucidate the microscopic origins of the enhanced catalytic performance of the PtCo/NPS catalysts relative to commercial Pt/C, density functional theory (DFT) calculations were performed. TEM and XRD analyses reveal that the PtCo/NPS catalyst exhibits an intermetallic structure with a Pt-enriched shell, which serves as the basis for constructing the PtCo@Pt model. Pt-alloy nanoparticles are known to develop Pt-enriched surface layers due to the lower surface energy of Pt and the partial dissolution of surface transition metals under operating conditions [72]. Accordingly, a single-layer Pt-skin model on an intermetallic core, denoted as PtCo@Pt (111), was constructed (Fig. S15).

To verify the thermodynamic structural stability and integrity of this Pt-skin architecture, we systematically evaluated the segregation energies (E_{seg}) within the PtCo@Pt slab (Fig. S16, Table S5). The segregation energy is defined as $E_{\text{seg}} = E_{\text{segregated}} - E_{\text{pristine}}$, where $E_{\text{segregated}}$ represents the total energy of the slab after interchanging atoms between adjacent layers, and E_{pristine} is the energy of the initial PtCo@Pt configuration. Positive E_{seg} values quantitatively indicate a thermodynamic preference for the pristine state. First, we examined the stability of the outermost Pt skin against the diffusion of subsurface Co atoms. The exposure of subsurface Co via an exchange with a surface skin Pt atom required a substantial thermodynamic penalty of +0.76 eV. This high positive E_{seg} value confirms that the Pt skin is remarkably stable and effectively suppresses the outward segregation of Co, which is crucial for preventing transition metal leaching during fuel cell operation. Furthermore, we evaluated the stability of the internal ordered structure by calculating atomic exchanges within the subsurface and core regions. Exchanging a subsurface Pt atom with a core Co atom yielded an E_{seg} of +0.39 eV, while the reverse exchange (subsurface Co with core Pt) necessitated an E_{seg} of +0.50 eV. The consistent positivity of these values indicates that the intermetallic PtCo core is thermodynamically robust and preferentially preserved, rather than structurally degrading or driving further subsurface reconstructions. Consequently, these rigorous thermodynamic assessments confirm that the core-shell-like PtCo@Pt structure is a highly stable configuration, validating its use as the representative model for our highly durable PtCo/NPS catalyst.

To clarify the role of NPS and validate PtCo@Pt (111) as the representative ORR-active surface, we evaluated O₂ and Co adsorption behaviors. On pyrrolic-N- and pyridinic-N-doped graphene, O₂ adsorption

induces spontaneous O—O bond dissociation, yielding excessively strong adsorption energies of -5.6 and -6.0 eV, respectively. The resulting $^*\text{O}$ species are therefore expected to bind too strongly to the carbon framework, creating a deep thermodynamic sink that hinders subsequent proton–electron transfer steps and increases the overpotential of the dissociative ORR pathway. In contrast, O_2 remains molecularly adsorbed on PtCo@Pt with a moderate adsorption energy of -0.2 eV, indicating that ORR occurs predominantly on the PtCo nanoparticle surface rather than on the N-doped carbon support. To assess the structural role of NPS, Co adsorption energies were calculated on pristine and pyrrolic-N-doped graphene. Co adsorption is thermodynamically unfavorable on pristine graphene ($+3.87$ eV) but favorable on pyrrolic-N-doped graphene (-0.43 eV), indicating that pyrrolic-N sites can effectively anchor PtCo nanoparticles. These results suggest that NPS primarily enhances catalyst stability through strengthened metal–support interactions, whereas the PtCo surface provides the main ORR-active sites.

Using this validated model, Gibbs free-energy diagrams were constructed to map the ORR pathways on both the pure Pt (111) and the PtCo@Pt (111) surfaces (Fig. 4a). While $\Delta G(^*\text{OOH})$ is similar for both surfaces, $\Delta G(^*\text{O})$ differs significantly by 0.63 eV. The $^*\text{O} \rightarrow ^*\text{OH}$ step is identified as the rate-determining step for Pt and the $^*\text{OH} \rightarrow \text{H}_2\text{O}$ step for PtCo@Pt (Fig. S17). The calculated overpotentials are 0.70 V for Pt and 0.36 V for PtCo@Pt, indicating substantially enhanced ORR kinetics. This improvement originates from the weakened $^*\text{O}$ adsorption induced by subsurface Co atoms.

To unravel the fundamental origin of the weakened $^*\text{O}$ binding, we evaluated the d-band center (ϵ_d) of clean Pt (111) and PtCo@Pt (111)

surfaces. According to the d-band model, subsurface Co induces compressive strain on the Pt skin and modifies the electronic structure via ligand effects. These combined effects result in a broadened d-band and a downward shift of ϵ_d relative to the Fermi level. The ϵ_d of PtCo@Pt is shifted to -1.98 eV, compared to -1.71 eV for Pt (111) (Fig. 4c). This shift increases the occupancy of antibonding states in the Pt—O interaction, thereby weakening the overall chemisorption strength.

Charge density difference (CDD) analysis shows reduced charge redistribution along the Pt—O bond on PtCo@Pt compared to Pt, indicating suppressed interfacial charge transfer (Fig. 4b, Fig. S18). This trend is further supported by projected density of states (PDOS) analysis, where the hybridization between O 2p and Pt 5d orbitals is significantly attenuated (Fig. 4d). The pure Pt (111) surface exhibits strong orbital hybridization between the O 2p and Pt 5d states near the Fermi level. In contrast, the PtCo@Pt surface displays a noticeable attenuation of this hybridization, which is mathematically validated by a reduced overlap metric (from 0.1279 for Pt to 0.0822 for PtCo@Pt) derived from the integration of the normalized Pt 5d and O 2p PDOS. Finally, to quantitatively evaluate the bonding strength, crystal orbital Hamilton population (COHP) and integrated COHP (ICOHP) analyses were performed using LOBSTER (Fig. 4e) [73]. The interaction between the adsorbed $^*\text{O}$ and the three adjacent Pt atoms at the FCC hollow site yielded an ICOHP value of -6.91 eV for Pt (111), whereas it shifted to -6.50 eV for PtCo@Pt. This less negative ICOHP value for PtCo@Pt provides definitive quantitative evidence of weakened Pt—O covalent bonding relative to pure Pt. The collective theoretical insights from E_{seg} , ϵ_d , CDD, PDOS, and COHP unequivocally demonstrate that the Pt-skin-terminated PtCo alloy optimally tailors the electronic structure, effectively weakening

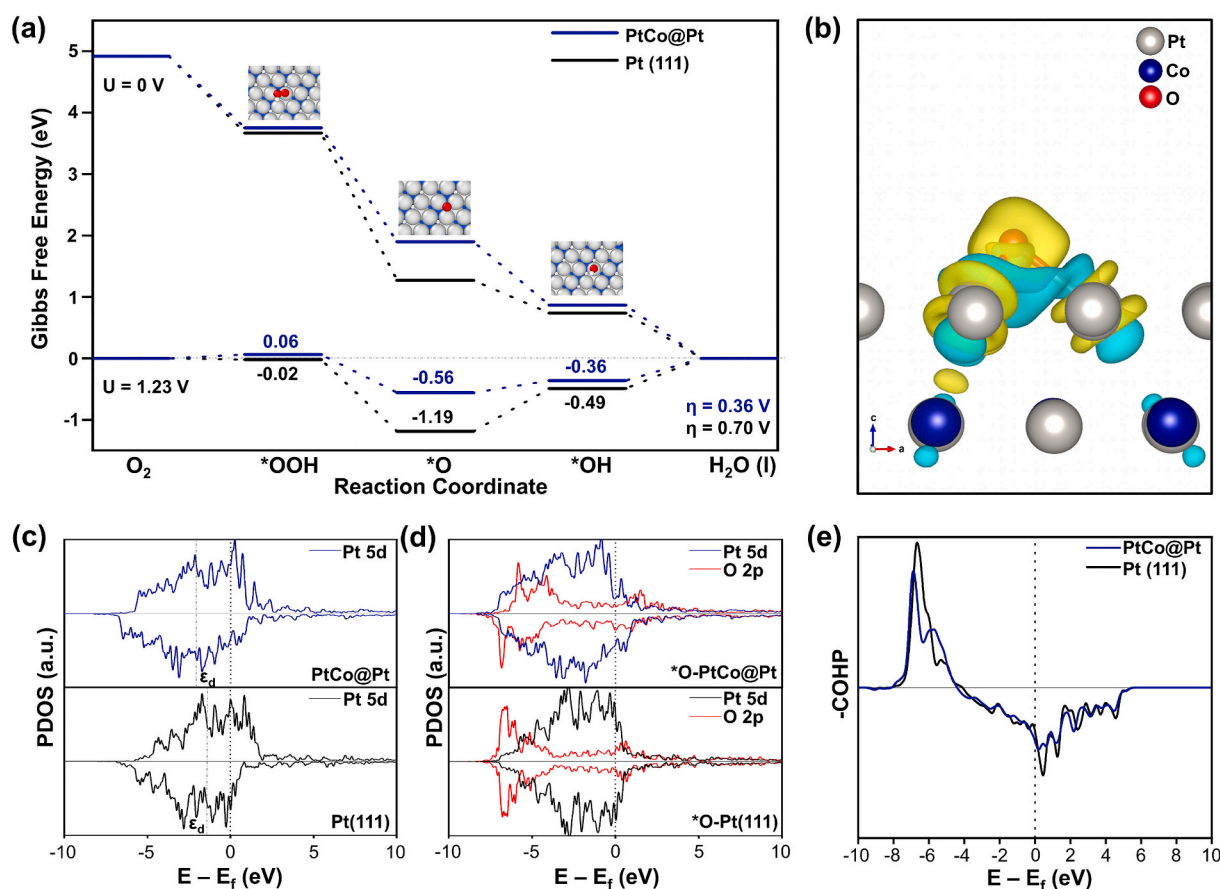


Fig. 4. (a) Calculated Gibbs free energy diagram for $4e^-$ ORR mechanism on the Pt (111) and PtCo@Pt (111). (b) Charge density difference of adsorbed oxygen and PtCo@Pt surface (isosurface level: $0.018 e \text{ Bohr}^{-3}$). (c) PDOS of Pt 5d orbital (surface Pt atoms). (d) PDOS of adsorbed $^*\text{O}$ (multiplied ten times for clarity) and surface Pt atoms (normalized per 16 surface Pt atoms) over -10 – 10 eV. (e) Crystal orbital Hamilton population (COHP) analysis for the oxygen adsorbed Pt (111) and PtCo@Pt.

the oxygen intermediate binding strength to drive the exceptional ORR activity observed experimentally.

Single-cell fuel cell performance and durability were evaluated using MEAs fabricated with PtCo/NPS0, PtCo/NPS3, and commercial Pt/C catalysts. The cathode Pt loading was $0.07 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ for PtCo/NPS0 and PtCo/NPS3, and $0.10 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ for Pt/C. All MEAs had an active area of 5 cm^2 , with commercial Pt/C ($0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) as the anode catalyst. The fuel cells were operated under fully humidified H_2/O_2 conditions at 1.5 bar backpressure. At beginning-of-lifetime (BOL), PtCo/NPS3 showed the highest mass activity of $0.84 \text{ A mg}_{\text{Pt}}^{-1}$ at 0.9 V, outperforming PtCo/NPS0 ($0.53 \text{ A mg}_{\text{Pt}}^{-1}$) and Pt/C ($0.21 \text{ A mg}_{\text{Pt}}^{-1}$), and exceeding the US DOE 2025 target ($0.44 \text{ A mg}_{\text{Pt}}^{-1}$) (Fig. 5a). The corresponding peak power densities reached 1180, 983, and 1076 mW cm^{-2} for PtCo/NPS3, PtCo/NPS0, and Pt/C, respectively (Fig. 5b). AST was performed by square-wave voltage cycling between 0.6 and 0.95 V for 30,000 cycles. After end-of-lifetime (EOL), PtCo/NPS3 retained a high mass activity of $0.65 \text{ A mg}_{\text{Pt}}^{-1}$, significantly higher than that of PtCo/NPS0 ($0.26 \text{ A mg}_{\text{Pt}}^{-1}$) and Pt/C ($0.07 \text{ A mg}_{\text{Pt}}^{-1}$) (Fig. 5c). The peak power densities decreased from 1180 to 1024 mW cm^{-2} for PtCo/NPS3, from 983 to 769 mW cm^{-2} for PtCo/NPS0, and from 1076 to 815 mW cm^{-2} for commercial Pt/C, corresponding to retention values of 86.8%, 78.2%, and 75.7%, respectively. These results highlight the superior performance and durability of PtCo/NPS3 as a cathode catalyst for PEMFC applications.

To further evaluate the practical water-management behavior of the NPS3-based catalyst layer, H_2/air single-cell tests were performed under fully humidified conditions (Fig. 5d-e). PtCo/NPS3 exhibited superior H_2/air polarization behavior over the full current-density range compared with PtCo/NPS0 and commercial Pt/C, even at a lower cathode Pt loading of $0.07 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. The maximum power density of PtCo/NPS3 reached 549 mW cm^{-2} at BOL and remained 376 mW cm^{-2} after 30,000 AST cycles. In contrast, commercial Pt/C decreased from 508 mW cm^{-2} to 323 mW cm^{-2} , while PtCo/NPS0 decreased from 348

mW cm^{-2} to 201 mW cm^{-2} . These results indicate that the increased hydrophilicity of NPS3 does not cause an evident flooding-induced mass-transport loss under the fully humidified H_2/air operating conditions used in this study. The improved H_2/air performance is consistent with more balanced wettability and effective ionomer accessibility within the catalyst layer.

In addition to the H_2/air assessment, the role of N-doping in the NPS support was further validated using a control catalyst prepared by depositing PtCo nanoparticles onto Vulcan carbon (PtCo/C, 20 wt% Pt and 6 wt% Co) with the same Pt loading ($0.10 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) as the commercial Pt/C (Fig. S19). Despite the identical Pt loading, PtCo/NPS3 exhibited superior performance, delivering higher mass activity and power density than PtCo/C. Notably, the mass activity and durability of this catalyst system surpass those of most previously reported catalysts (Table S6). To further evaluate the catalyst performance under a more representative cathode loading, additional MEA tests were performed at $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$, where PtCo/NPS3 still exhibited superior performance compared with commercial Pt/C (Fig. S20).

The differences in performance are likely related to the surface characteristics of the carbon supports, particularly the presence of N species. N-doping is widely recognized for enhancing the interaction between the carbon surface and ionomers, which can improve catalyst layer morphology and facilitate proton transport [22,49,74]. To examine this effect, water contact angle measurements were performed on carbon films composed of Vulcan, NPS0, and NPS3 (Fig. 6a-c). The measured contact angles were 146° , 154° , and 135° for Vulcan, NPS0, and NPS3, respectively, indicating that NPS3 possesses a more hydrophilic surface. While excessively hydrophilic surfaces may lead to flooding at high current densities, a moderately hydrophilic character is beneficial for ionomer dispersion and the formation of an efficient triple-phase boundary [75]. The intermediate wettability of NPS3 therefore suggests an optimal balance between water management and ionomer accessibility.

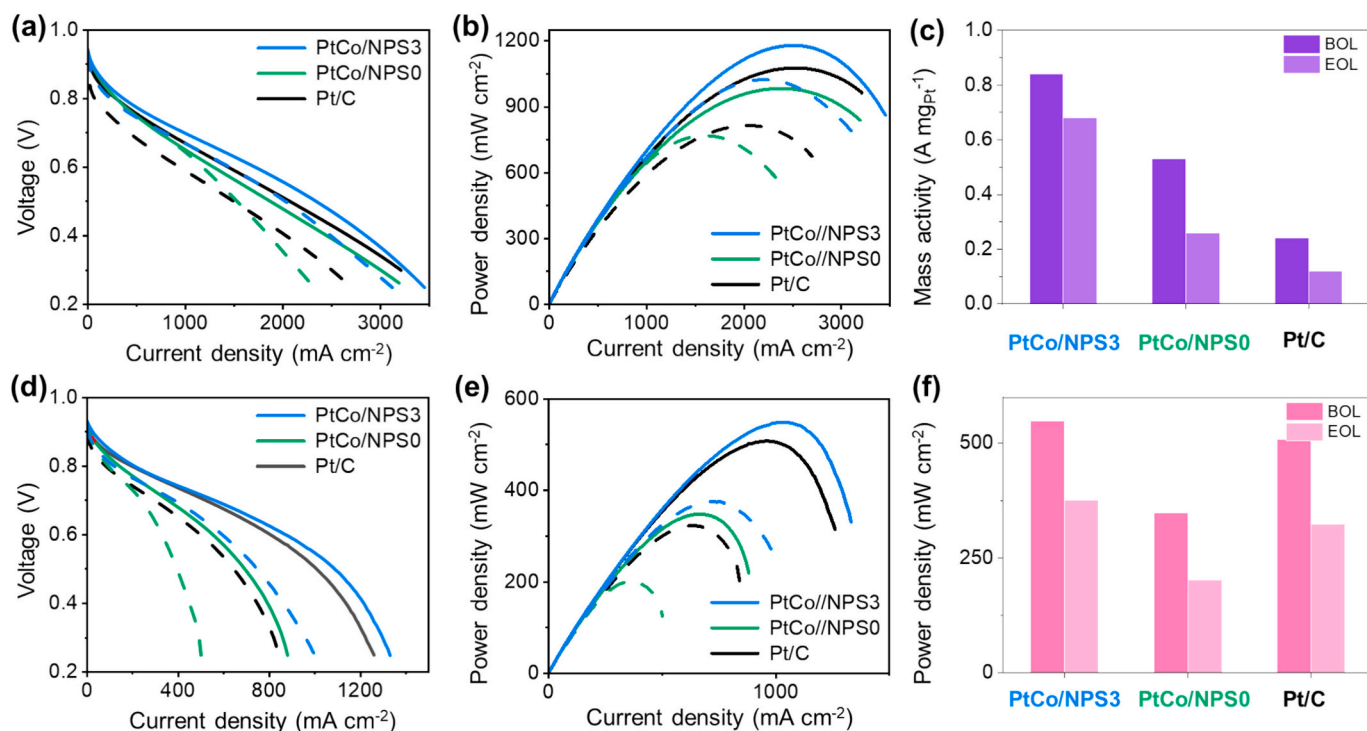


Fig. 5. PEMFC performance of PtCo/NPS3, PtCo/NPS0, and commercial Pt/C. (a) H_2/O_2 polarization curves, (b) corresponding power density curves, and (c) BOL and EOL mass activities at 0.9 V. (d) H_2/air polarization curves, (e) corresponding power density curves, and (f) BOL and EOL peak power densities. Solid and dashed lines indicate BOL and EOL, respectively. The anode was 20 wt% Pt/C with a Pt loading of $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. The cathode Pt loading was $0.07 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ for PtCo/NPS0 and PtCo/NPS3 and $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ for commercial Pt/C. Durability testing was performed using a square-wave protocol between 0.6 and 0.95 V with a dwell time of 3 s at each potential.

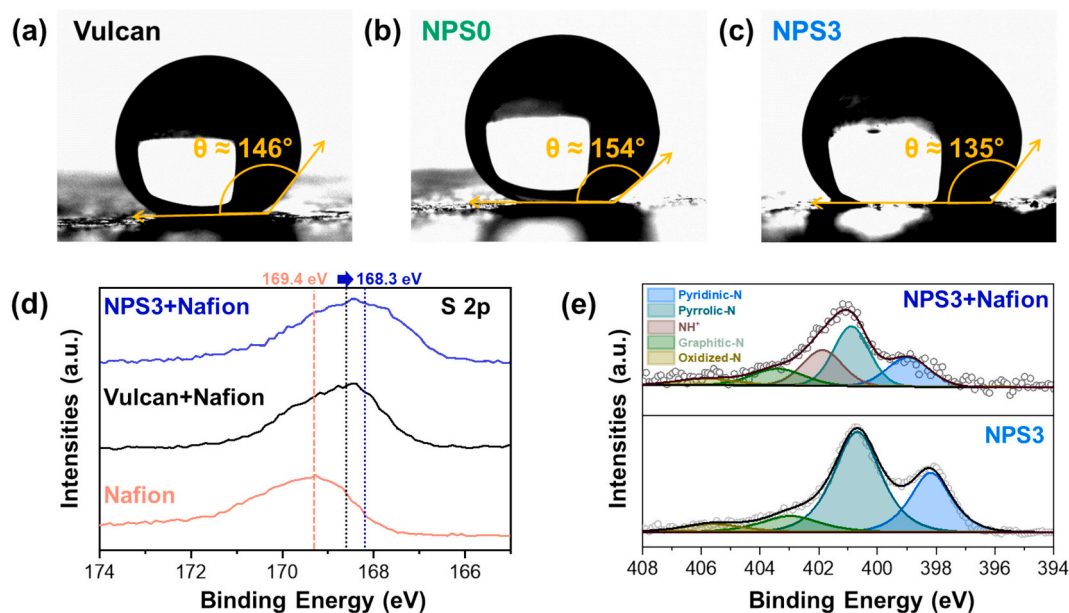


Fig. 6. Water contact angle measurements for carbon films composed of (a) Vulcan, (b) NPS0, and (c) NPS3. XPS spectra of (d) S 2p and (e) N 1s for physical mixtures of the carbons with Nafion ionomer.

To further investigate possible interactions between the carbon surface and the Nafion ionomer, XPS measurements were performed on physical mixtures of the carbon materials with Nafion (Fig. 6d-e). In the S 2p spectra, NPS3 exhibited a pronounced binding-energy shift from 169.4 eV for free Nafion to 168.3 eV, which is substantially larger than the slight shift observed for Vulcan. This negative shift suggests strong acid–base interactions between the sulfonic groups of the ionomer and the basic N functionalities on the N-doped carbon surface [76,77]. In parallel, the N 1s spectra of NPS3 mixed with ionomer revealed the appearance of a new component at ~ 401.6 eV, which can be assigned to protonated N species (NH^+) and is absent in pristine NPS3. The simultaneous observation of the S 2p shift and the NH^+ feature is consistent with proton transfer from the sulfonic acid groups to N sites, supporting the proposed acid–base interaction mechanism. These XPS results indicate that N doping strengthens the interfacial interaction with the ionomer compared to undoped carbons, which can facilitate more uniform ionomer distribution, improved triple-phase boundary formation, and enhanced proton transport within the catalyst layer. To directly visualize the spatial distribution of the ionomer within the catalyst layer, Microtomed HAADF-STEM and EDS elemental mapping were performed after ionomer incorporation (Fig. S21). Since fluorine (F) mainly originates from the Nafion ionomer, the F signal was used as an indicator of ionomer distribution. Compared with PtCo/NPS0, PtCo/NPS3 exhibited a more homogeneous F distribution within the imaged microtomed catalyst-layer regions, whereas PtCo/NPS0 showed locally concentrated F-rich regions. These results suggest improved ionomer dispersion on the N-doped carbon support. The EDS observations are consistent with the XPS results and suggest that acid–base interactions between the N functionalities and sulfonic acid groups contribute to the improved ionomer distribution.

4. Conclusions

In this work, we developed N-doped carbon supports derived from upcycled PS via a facile one-pot crosslinking and N-doping strategy. The supports were constructed via a Friedel–Crafts reaction followed by carbonization and exhibit tunable N content with tailored surface functionalities. N doping enables uniform ionomer distribution and promotes strong coordination between Co species and N functionalities, providing robust anchoring sites for the formation of ordered

intermetallic PtCo nanoparticles. DFT calculations provide additional insight by evaluating the adsorption energetics of oxygen intermediates on PtCo surfaces, supporting the experimentally observed enhancement in ORR activity. These combined structural and interfacial features strengthen metal–support interactions and improve oxygen accessibility within the catalyst layer, thereby enhancing both catalytic activity and durability. PtCo/NPS3 delivers a mass activity of $0.84 \text{ A mg}_{\text{Pt}}^{-1}$ at 0.9 V and retains $0.65 \text{ A mg}_{\text{Pt}}^{-1}$ after AST. In MEA tests, it achieves a peak power density of 1180 mW cm^{-2} and maintains 86.8% of its initial performance after 30,000 cycles. These results demonstrate that PtCo/NPS3 is a cost-effective and durable PEMFC catalyst, while highlighting plastic-waste upcycling as a viable strategy for scalable, high-performance fuel cell systems.

CRedit authorship contribution statement

Yewon Kim: Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Daehyeon Seo:** Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Min Seo Kim:** Formal analysis. **Su Min Ahn:** Formal analysis. **Se Youn Cho:** Formal analysis. **Yunji Kim:** Formal analysis. **Jiho Choi:** Formal analysis. **Byung-Hyun Kim:** Writing – review & editing, Formal analysis, Data curation, Conceptualization. **Hongseok Yun:** Writing – original draft, Data curation, Conceptualization. **Young Jun Lee:** Writing – review & editing, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.180588>.

Data availability

Data will be made available on request.

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