



A platinum catalyst with hierarchical porosity supported on a honeycomb-like nitrogen-doped carbon for excellent oxygen reduction reaction performance

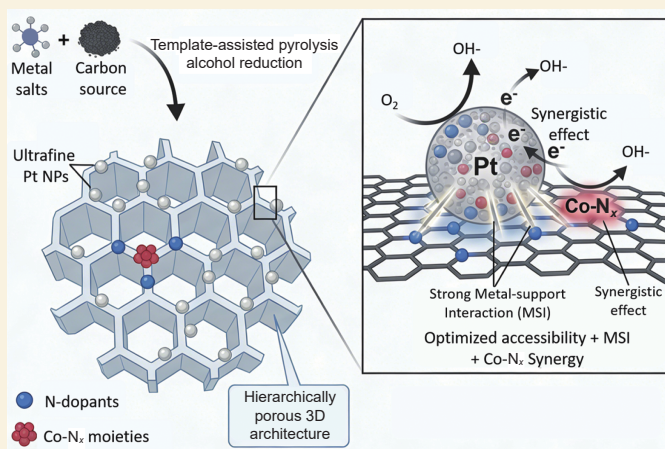
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Abstract: Advanced catalyst structures with good active site accessibility and strong metal-support interactions are crucial for oxygen reduction reaction (ORR) catalysis. A hierarchically porous Pt catalyst supported on honeycomb-like nitrogen-doped carbon (Pt/HNC-400, where 400 denotes the optimal dosage (mg) of the sacrificial SiO₂ hard template used during synthesis) was fabricated by combining template-assisted pyrolysis and alcohol reduction. The fabrication involves the template-assisted pyrolysis of ZIF-67 (which provides the N-dopant through its 2-methylimidazole ligand) followed by HF etching to completely remove the SiO₂, yielding a 3D interconnected porous carbon support. Compared to a commercial Pt/C, it had an exceptional ORR performance with a half-wave potential of 0.901 V (41 mV higher), a mass activity at 0.9 V that was 15.3 times higher, and significantly improved durability (a half-wave potential decay of 25 mV vs. 80 mV after 10 000 accelerated durability tests (ADTs)). Mechanistic investigations showed that this superior performance is due to the combined effects of the 3D porous structure, ultrafine Pt nanoparticles with strong metal-support interactions, and in-situ formed Co-N_x moieties from the pyrolysis of precursor ZIF-67. After 10 000 ADTs it was shown to have excellent structural integrity, retaining 87.4% of its initial electrochemically active surface area (102.7 m²g⁻¹). This study may assist the development of new high-performance ORR catalysts.

Key words: Oxygen reduction reaction; honeycomb-like carbon; template-assisted pyrolysis; nitrogen-doped carbon; ZIF-67



1 Introduction

In recent years, growing global environmental concerns and the escalating energy crisis have significantly increased the demand for advanced energy devices, thereby driving the rapid development of electrochemical energy storage systems^[1]. Fuel cells, widely recognized as one of the most promising energy conversion technologies^[2], have attracted extensive attention due to their environmentally friendly operation and high energy density^[3]. However, despite their great potential, several critical challenges persist, hindering their large-scale application and commercialization^[4]. A major bottleneck in fuel cell techno-

logy is the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode, which stands in sharp contrast to the relatively facile hydrogen oxidation reaction (HOR) at the anode^[5–7]. This difference stems from the complex multi-step mechanism of ORR, which involves the formation and transformation of various intermediate species^[8]. Consequently, extensive research efforts have been devoted to understand-

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ing the ORR process and developing efficient ORR catalysts.

Among the numerous electrocatalysts reported in the literature, metal-based catalysts supported on porous carbon materials have emerged as a research focus^[9]. These composite catalysts leverage the unique properties of porous carbon, including its large specific surface area^[10–11] and interconnected conductive network^[12]. The high specific surface area of porous carbon enables the efficient adsorption of oxygen molecules onto the catalyst surface, thereby enhancing reaction kinetics and catalyst utilization^[13–14]. Furthermore, the porous structure facilitates the diffusion of reactants and products through its hierarchical channels^[15], inhibits the accumulation of reaction intermediates, and preserves the catalyst's structural integrity during operation^[16]. Collectively, these characteristics render metal-porous carbon catalysts highly promising candidates for boosting the performance and durability of fuel cells^[16–17].

Currently, commercial Pt/C catalysts predominantly utilize several types of carbon blacks, as support materials, including acetylene black, Ketjen Black, Black Pearl, and Vulcan XC-72. Despite their large specific surface areas, these carbon blacks suffer from poor thermal stability at elevated temperatures^[18]. Their surfaces are characterized by numerous defects, unsaturated bonds, and oxygen-containing functional groups. In addition, the harsh operating environment of proton exchange membrane fuel cells exacerbates the corrosion rate^[19], weakening the interaction between the carbon black support and Pt nanoparticles^[20]. This degradation process ultimately leads to structural collapse, Pt loss, and a significant reduction in both catalytic activity and stability. Metal oxides such as CeO₂, TiO₂, and ZrO₂ have emerged as potential support materials for ORR catalysts due to their favorable thermal stability and electrical conductivity^[21]. However, their relatively small specific surface areas pose a challenge, as they can limit the number of active sites available for the ORR, thereby affecting overall catalyst performance.

To address these limitations and enhance the performance of ORR catalysts at the cathode, research-

ers are actively exploring the development of novel support materials and optimizing preparation methodologies^[22–24]. The primary focus lies in maximizing specific surface area, electrical conductivity, and thermal stability to facilitate more efficient electron transfer and better utilization of active sites^[22–23,25]. ZIF-67-derived carbon, a cutting-edge carbon-based material synthesized through the high-temperature pyrolysis of ZIF-67, has garnered significant attention in the electrochemical field. This material offers a combination of high specific surface area ($>1500 \text{ m}^2/\text{g}$)^[25], excellent electrical conductivity (3.2 S/cm)^[23], and superior thermal stability (up to $800 \text{ }^\circ\text{C}$)^[22], making it an ideal candidate for use as a support material. In the context of PEMFCs, ZIF-67-derived carbon provides abundant active sites and efficient electron transport pathways, thereby enhancing both the activity and durability of ORR catalysts^[26]. Furthermore, its highly porous structure and tunable pore size distribution allow for customization to meet the specific requirements of ORR catalysts, enabling the achievement of optimal catalytic performance. While recent studies have explored Pt nanoparticles supported on ZIF-derived porous carbons, most reports focus on conventional polyhedral morphologies derived from template-free pyrolysis, which often suffer from limited pore connectivity and suboptimal mass transport. In contrast, our template-assisted strategy using optimized SiO₂ amounts (400 mg) yields a unique honeycomb-like architecture with three-dimensional (3D) interconnected hierarchical pores. This structural design not only maximizes Pt dispersion ($2.8 \pm 0.3 \text{ nm}$) and metal-support interactions but also provides superior mass transport pathways, outperforming previously reported ZIF-derived Pt catalysts in terms of both half-wave potential and durability.

In this study, a template-assisted pyrolysis strategy was developed for the synthesis of honeycomb-like nitrogen-doped carbon (HNC) featuring a 3D cross-linked hierarchical pore structure. This method involves the direct pyrolysis of ZIF-67 intermediates, which are subsequently utilized as supporting materials for Pt loading. The ethylene glycol re-

duction method was applied to deposit Pt nanoparticles onto the HNC support, ultimately yielding the honeycomb carbon-supported platinum catalyst Pt/HNC. The unique structural design of HNC endows it with the ability to effectively disperse and utilize Pt nanoparticles. This architecture facilitates a more rapid mass transfer process, enhancing both the diffusion and transmission efficiency within the catalyst. Notably, the Co-N_x functional groups inherent in HNC can serve as active centers, significantly contributing to the improvement of the ORR performance and stability of the catalyst. As a result, the as-prepared Pt/HNC catalyst demonstrated outstanding ORR catalytic performance and remarkable stability. This innovative approach provides a novel perspective for the fabrication of high-performance ORR catalysts using ZIF-derived materials, opening up new avenues for the development of advanced electrocatalysts in fuel cell applications.

2 Experiment

2.1 Synthesis of SiO₂ template

A typical sol-gel procedure was employed to synthesize the SiO₂ nanoparticles. Briefly, 225 mL of absolute ethanol, 30 mL of deionized water, and 6 mL of ammonia solution were stirred for 10 min. Then, 10 mL of tetraethyl orthosilicate (TEOS) was added dropwise over 15 min. After stirring for 2 h at room temperature, the milky white colloidal solution was centrifuged at 8000 r/min for 5 min. The resulting precipitate was washed with water and ethanol, and dried in a vacuum oven at 60 °C for 12 h to yield the SiO₂ powder.

2.2 Synthesis of HNC

For the synthesis of HNC, 0.87 g of Co(NO₃)₂·6H₂O and a certain amount of as-prepared SiO₂ nanoparticles were dissolved in 50 mL of methanol. Separately, 1.5 g of 2-methylimidazole was dissolved in 30 mL of methanol. The 2-methylimidazole solution was added to the Co(NO₃)₂-SiO₂ mixture under stirring at 60 °C until the methanol evaporated, forming a purple solid. After drying and grinding, SiO₂@ZIF-67 was obtained and annealed at 500 °C

for 2 h in N₂ with a heating rate of 5 °C/min. Post-annealing the product was treated with 10% HF for 12 h to remove SiO₂. After centrifugation, washing, and drying at 80 °C, HNC was obtained. To investigate the effect of the SiO₂ amount on the final product morphology and properties, three different amounts of SiO₂ (100, 400, and 700 mg) were used in the synthesis, and the resulting products were named HNC-100, HNC-400 and HNC-700, respectively. The SiO₂ dosages of 100, 400, and 700 mg were selected based on preliminary optimization experiments. Lower SiO₂ content (100 mg) resulted in insufficient pore formation, whereas excessive SiO₂ (700 mg) led to partial structural collapse of the carbon framework. The intermediate dosage (400 mg) achieved the optimal balance, yielding the highest BET surface area and well-developed hierarchical porosity, consistent with the principle that template content critically governs pore architecture in MOF-derived carbons.

2.3 Synthesis of Pt/HNC

The Pt/HNC catalyst was synthesized by the ethylene glycol reduction method (Fig. 1). First, 60 mg of HNC was added to a 1 : 1 (v/v) ethylene glycol-deionized water mixture in Beaker A and ultrasonicated for 1 h. In Beaker B, 2 mL of H₂PtCl₆·6H₂O solution and 20 mL of ethylene glycol were mixed dropwise and sonicated for 15 min. The solution from Beaker B was transferred to Beaker A, mixed thoroughly, and the pH of the mixture was adjusted to 10 using 1 mol/L NaOH. After refluxing at 160 °C for 3 h in an oil bath, the mixture was cooled to 40 °C, its pH was adjusted to 2, and the mixture was stirred for 10 h. The Pt/HNC catalyst was collected by centrifugation, washed repeatedly, and dried at 80 °C for 12 h. Corresponding catalysts were prepared using HNC-100, HNC-400 and HNC-700 as supports, and labeled as Pt/HNC-100, Pt/HNC-400 and Pt/HNC-700, respectively.

For comparative analysis, the Pt/CNC catalyst was also synthesized. The preparation of polyhedral SiO₂/ZIF-67 intermediates followed the previous protocol, except that the stirring and evaporation times were extended to 6 h to form well-defined polyhedral

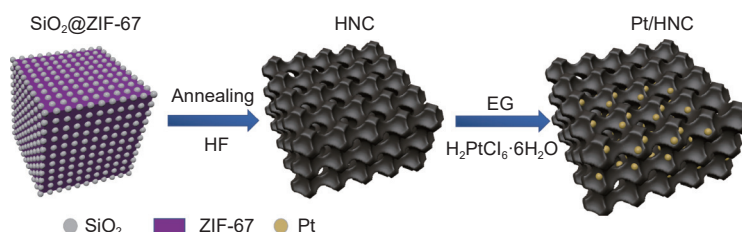


Fig. 1 Schematic illustration of the fabrication process of the Pt/HNC catalyst

structures. Separately, ZIF-67 was synthesized by adding 2-methylimidazole solution to a $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution, stirring for 0.5 h, and standing for 5 h. After centrifugation and drying, ZIF-67 powder was obtained. CNC was then prepared by calcining the intermediate under the same conditions as those for HNC. The Pt/CNC catalyst was fabricated by the ethylene glycol reduction method with CNC replacing HNC. After synthesis, Pt/CNC was centrifuged, washed until neutral pH was achieved, and dried at 80 °C.

2.4 Physical characterization

A scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS, HORIBA E-MAX) and a JEOL JEM-2010 transmission electron microscope (TEM) were used to observe the morphology, elemental mapping, and microstructure of the various carbons and catalysts produced. Bruker D8 Advanced X-ray diffraction (XRD) with $\text{Cu K}\alpha_1$ radiation ($\lambda = 0.15 \text{ nm}$) was employed to determine the crystal structures of the catalysts. An Escalab 250X X-ray photoelectron spectroscopy (XPS) instrument was utilized to analyze the elemental composition and valence states of the prepared samples. Micromeritics ASAP 2460 BET was adopted to measure and analyze the specific surface area and pore size distribution of the different carbons and catalysts.

2.5 Electrochemical characterization

All electrochemical tests were conducted using a three-electrode system, where the working electrode was a glassy carbon electrode with an area of 0.0707 cm^2 . A CHI760E potentiostat/galvanostat was employed to control the current and voltage. The ink for electrochemical tests was prepared with a catalyst-to-ionomer mass ratio of 2 : 1. An appropriate amount

of the ink was then drop-cast onto a rotating disk electrode (RDE) to ensure a Pt loading density of $25 \mu\text{g}/\text{cm}^2$. Subsequently, 50 cyclic voltammetry (CV) cycles were performed to activate the catalyst in a 0.1 mol/L N_2 -saturated HClO_4 electrolyte at room temperature, within a potential range of 0.05–1.5 V (vs. RHE) and a scan rate of 200 mV/s. To ensure accurate determination of the electrochemically active surface area (ECSA) for Pt, the CV curves were background-subtracted using the corresponding HNC support measured under identical conditions. This correction effectively eliminates any contribution from Co-related redox features in the Hupd region, ensuring that the calculated ECSA values exclusively reflect the Pt active sites.

CV curves were obtained in a 0.1 mol/L N_2 -saturated HClO_4 solution, scanning from 0.05–1.1 V (vs. RHE) at a scan rate of 50 mV/s. Linear sweep voltammetry (LSV) curves were recorded in a 0.1 mol/L O_2 -saturated HClO_4 solution, scanning from 0.05–1.1 V (vs. RHE) at a scan rate of 10 mV/s. Accelerated durability tests were carried out to evaluate the catalytic durability. In a 0.1 mol/L O_2 -saturated HClO_4 solution, multiple CV cycles were performed between 0.6 and 1.1 V (vs. RHE) at a scan rate of 200 mV/s. The electrocatalytic performance of the Pt/HNC catalyst was further characterized by Tafel analysis, electrochemical impedance spectroscopy (EIS), and chronoamperometric (i-t) tests using a three-electrode electrochemical workstation. First, high-purity argon was continuously bubbled into the electrolyte for 1 h through a gas purging inlet directly immersed in the solution. The outlet tube was connected to maintain a gas flow rate of 20–50 mL/min for saturation, followed by CV tests of the catalyst. Subsequently, high-purity oxygen was purged for 1 h to achieve saturation.

tion, and Tafel, EIS, and i-t tests were conducted in the O₂-saturated electrolyte. During these tests, oxygen was continuously and gently bubbled into the electrolyte to maintain O₂ saturation. The ORR mechanism was investigated by rotating ring disk electrode (RRDE) and RDE tests. The ORR is governed by both kinetic and oxygen diffusion processes, with diffusion control dominating at low potentials and kinetic control at high potentials. The RDE was maintained at a stable rotational speed during testing, and RDE tests were conducted at rotational speeds ranging from 900 to 2500 r/min with a scan rate of 5 mV/s.

3 Results and discussion

3.1 Microstructure analysis

The XRD patterns of the Pt/HNC-100, Pt/HNC-400, and Pt/HNC-700 catalysts are depicted in Fig. 2. A prominent broad diffraction peak at 25° in all 3 samples corresponds to the (002) plane of amorphous carbon, confirming the successful transformation of ZIF-67 into disordered carbon. Four characteristic diffraction peaks at 39.8°, 46.3°, 67.5° and 81.7° are indexed to the (111), (200), (220) and (311) planes of Pt (PDF #04-002-0887), respectively, while the peaks at 44.3°, 51.4° and 76.0° are attributed to the (111), (200) and (220) planes of Co (PDF #00-015-0806), clearly indicating the successful loading of Pt nanoparticles. Notably, the Pt peak intensity increases and the peak half-width decreases with increasing SiO₂ content, suggesting improved crystallinity and larger Pt nanoparticles. This phenomenon can be attributed to the templating effect of SiO₂, which creates hier-

archical pore structures that regulate the dispersion of metal precursors during synthesis, as demonstrated in recent work on mesoporous catalyst design^[27]. Morphological analysis by SEM (Fig. S3) reveals distinct structural evolution: Pt/HNC-100 exhibits an irregular morphology, which may induce lattice strain and size-dependent peak shifts in Pt nanoparticles. In contrast, Pt/HNC-400 and Pt/HNC-700 feature three-dimensional (3D) cross-linked pore architectures with reduced defect density. Such structural ordering at elevated pyrolysis temperatures has been shown to minimize lattice distortion in supported metal nanoparticles^[28], explaining the negligible changes in their diffraction patterns.

Fig. 3 depicts the elemental composition and corresponding spatial distribution of Pt/HNC-400. The homogeneous dispersion of N, O, Co and Pt elements across the cellular carbon framework (Fig. 3b-e) confirms the effective integration of heteroatoms and metal species during the pyrolysis-etching process. This structural homogeneity is critical for creating accessible active sites in heterogeneous catalysis.

TEM images in Fig. 4 reveal well-dispersed Pt nanoparticles (NPs) on the carbon matrix with negligible agglomeration, consistent with the morphological features observed by SEM (Fig. S3). Statistical analysis of 200 randomly selected Pt NPs (Fig. 4b) yields a narrow size distribution centered at 2.8 ± 0.3 nm (mean $\pm$ standard deviation), a dimension approaching the optimal range (<3 nm) for maximizing surface-to-volume ratios in noble metal catalysts. The inverse correlation between Pt NP size and catalytic activity can be rationalized by the increased density of undercoordinated surface atoms in smaller NPs, which typically enhances the adsorption and activation of reactant molecules.

Fig. 4c illustrates the residual pores after the etching process, highlighted by a yellow ring. These interconnected channels, formed during the controlled thermal decomposition of ZIF-67/SiO₂ composites, create a hierarchical porosity that synergistically enhances mass transport and active site accessibility. Such an architecture aligns with the design prin-

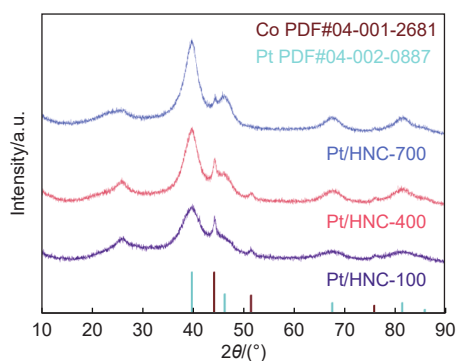


Fig. 2 XRD patterns of the Pt/HNC-100, Pt/HNC-400 and Pt/HNC-700 catalysts

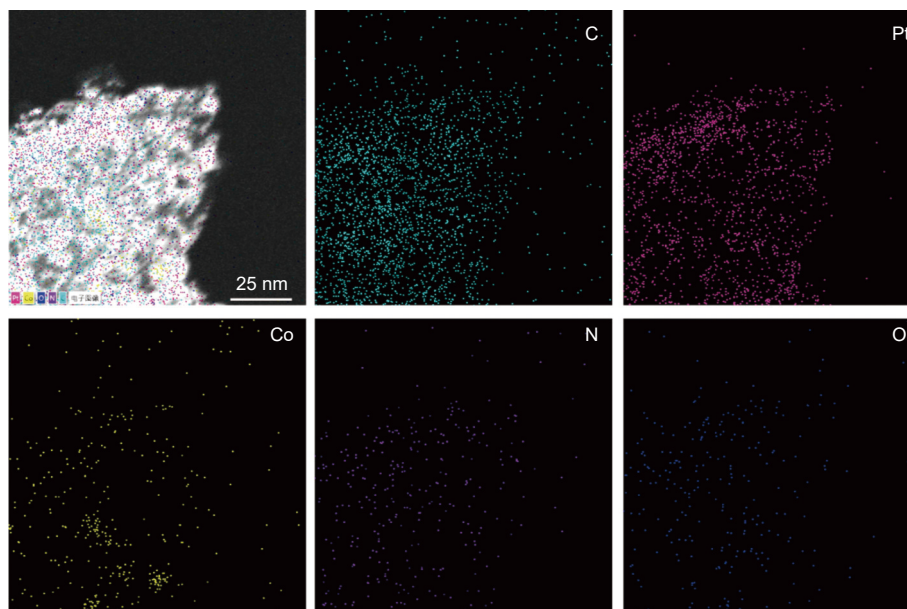


Fig. 3 Elemental mapping results of C, Pt, Co, N and O in the Pt/HNC-400 catalyst

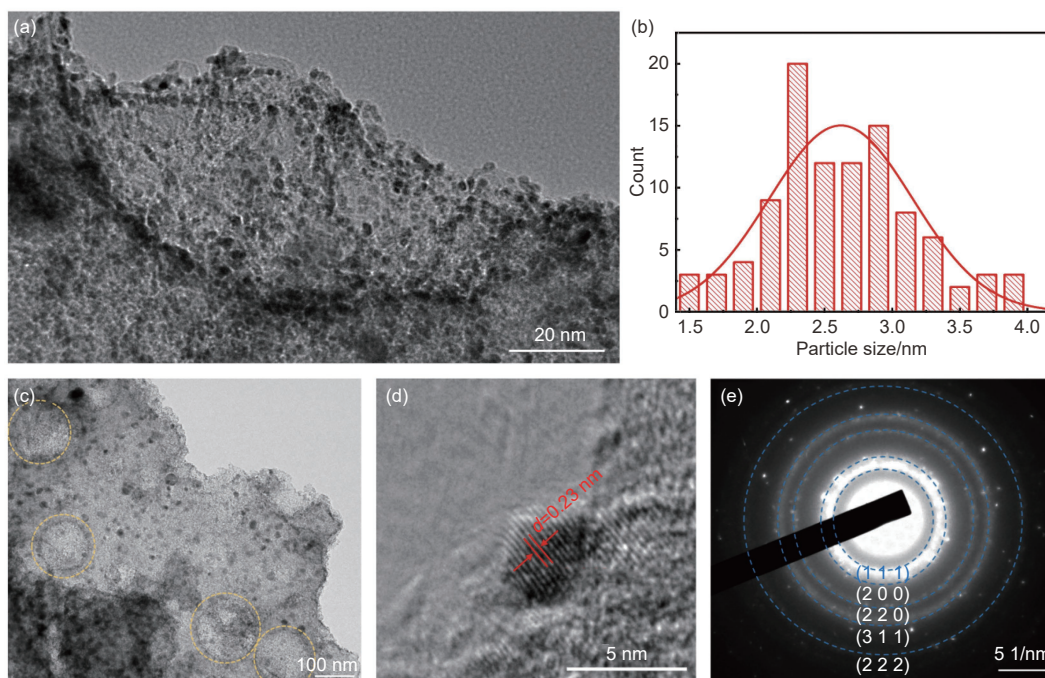


Fig. 4 (a) TEM image of Pt/HNC-400 showing well-dispersed Pt nanoparticles on the carbon matrix. (b) Particle size distribution histogram based on statistical analysis of 200 randomly selected Pt nanoparticles, yielding a mean diameter of 2.8 ± 0.3 nm. (c) HRTEM image showing residual pores after etching (highlighted by yellow ring). (d) High-resolution TEM image revealing lattice fringes with a spacing of 0.23 nm corresponding to Pt (111) plane. (e) Selected-area electron diffraction (SAED) pattern confirming the amorphous nature of the carbon matrix

ciples for advanced electrocatalysts, where multimodal pore systems optimize reactant diffusion and intermediate stabilization.

Atomic-scale characterization by high-resolution TEM (HRTEM) (Fig. 4d) reveals distinct lattice fringes with a spacing of 0.23 nm, corresponding to the (111) crystallographic plane of face-centered cu-

bic Pt (JCPDS 04-002-0887). The selected-area electron diffraction (SAED) pattern (Fig. 4e) displays diffuse concentric rings rather than discrete diffraction spots, confirming the amorphous nature of the carbon matrix. This structural feature, combined with the absence of crystalline metal oxide diffraction signals in the SAED pattern, corroborates the XRD (Fig. 2) and

XPS (Fig. S4) analyses. Collectively, these results verify the successful immobilization of metallic Pt NPs on defect-rich carbon by the ethylene glycol reduction method.

The architectural porosity and interfacial characteristics of catalyst supports fundamentally govern their electrocatalytic performance by modulating active-site accessibility and mass-transport kinetics. Nitrogen physisorption analysis (Fig. S5) reveals that HNC-100, HNC-400 and HNC-700 exhibit type IV isotherms with H3-type hysteresis loops, characteristic of mesoporous materials with slit-shaped pores. A narrow pore-size distribution centered at 9 nm (inset, Fig. S5) confirms the uniform mesoporosity generated through the SiO₂ templating strategy, consistent with recent advances in the confined-space carbonization of metal-organic frameworks.

The BET specific surface areas of HNC-100, HNC-400 and HNC-700 were determined to be 195.4, 435.1 and 297.1 m²/g, respectively. The BET surface area increases progressively from 195.4 (HNC-100) to 435.1 m²/g (HNC-400) and then decreases to 297.1 m²/g for HNC-700. The superior surface area of HNC-400 originates from its dual-scale porosity: (1) residual micropores (< 2 nm) inherited from the ZIF-67 precursor and (2) engineered mesopores (~ 9 nm) created by SiO₂ etching. This hierarchical architecture provides maximized Pt nanoparticle anchoring sites while maintaining efficient reactant diffusion pathways a critical design principle for high-performance ORR catalysts. The direct correlation between BET surface area and Pt loading (Table 1) provides unambiguous evidence that the hierarchical pore architecture is essential for achieving high-density Pt anchoring. Furthermore, the superior mass activity and kinetic parameters of Pt/HNC-400 directly reflect the benefits of this optimized porous structure in facilitating triple-phase boundary reactions.

Table 1 Pt content of the Pt/HNC-100, Pt/HNC-400 and Pt/HNC-700 catalysts, determined from ICP-OES tests

Catalysts	Pt/HNC-100	Pt/HNC-400	Pt/HNC-700
Pt/%	13.8	16.7	15.3

Notably, the ultrahigh surface area of HNC-400 (435.1 m²/g) exceeds values reported for most Pt-supported carbon materials (typically 200-350 m²/g), suggesting exceptional potential for interfacial oxygen activation. This structural superiority directly contributes to improved ORR activity by (1) exposing abundant triple-phase boundaries for O₂ adsorption and (2) facilitating rapid proton/electron transfer through interconnected conductive networks.

Quantitative elemental analysis by inductively coupled plasma optical emission spectrometry (ICP-OES) reveals distinct variations in Pt mass loading among the catalysts (Table 1). Pt/HNC-400 exhibits superior metal utilization efficiency with a Pt loading of 16.7%, which is significantly higher than those of Pt/HNC-700 (15.3%) and Pt/HNC-100 (13.8%). This loading hierarchy correlates directly with the BET specific surface area sequence (435.1 vs. 297.1 vs. 195.4 m²/g), confirming the critical role of substrate porosity in regulating metal dispersion through spatial confinement effects.

The 23.5% enhancement in Pt loading of HNC-400 compared to HNC-100 stems from its dual-scale porous architecture: (1) microporous domains (< 2 nm) that provide high-density anchoring sites by strong metal-support interactions, and (2) mesoporous channels (~ 9 nm) that facilitate precursor infiltration during wet-chemical deposition. Notably, the decreased Pt loading in HNC-700 despite its moderate surface area suggests competing mechanisms at elevated temperatures, including partial pore collapse and reduced surface oxygen functionalities, both of which are critical for Pt ion adsorption.

XPS results (Fig. 5) confirm the coexistence of Pt, Co, C, N and O in the Pt/HNC-400 catalyst, which is consistent with both the SEM-EDS mapping results (Fig. 2) and the reference spectrum of HNC-400 (Fig. S4). This consistency validates the structural integrity of the support during Pt deposition. Notably, the peak shift and reduced binding energy observed in the high-resolution Pt 4f spectrum of Pt/HNC-400 can be attributed to electron transfer from HNC to Pt, as well as the strong interaction between Pt and HNC^[29]. The

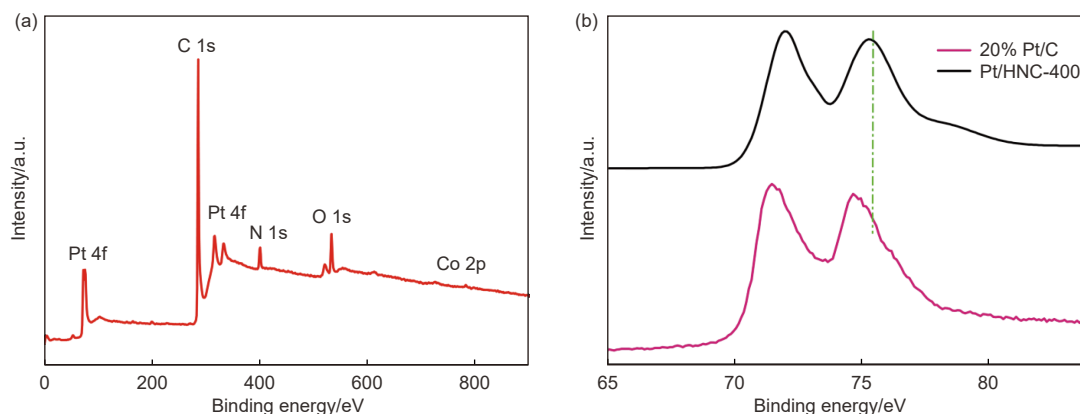


Fig. 5 (a) XPS survey spectra of the Pt/HNC-400 catalyst, and (b) magnified spectra of Pt 4f

negative shift in Pt 4f binding energy provides direct evidence of strong electronic interaction between Pt and the Co,N-codoped carbon support. This electron donation from support to Pt optimizes the d-band center of Pt, weakening oxygen intermediate adsorption and accelerating ORR kinetics consistent with the superior mass activity (1.84 A/mg) and small Tafel slope (58.8 mV/dec) observed for Pt/HNC-400. This interaction facilitates the effective anchoring of Pt nanoparticles and suppresses their aggregation, thereby enhancing the catalytic performance of the catalyst.

3.2 Electrochemical performance

The synergistic structural advantages of HNC-400, characterized by its hierarchical porosity (435.1 m²/g) and atomic Co-N_x coordination motifs (XPS, Fig. 3d), motivated a systematic evaluation of its ORR activity. The electrocatalytic performance of HNC-400 toward the ORR was investigated in 0.1 mol/L HClO₄ electrolyte using CV and LSV with a RDE configuration. As shown in Fig. S6a, the CV curve obtained in O₂-saturated electrolyte exhibits a well-defined cathodic peak at 0.59 V (vs. RHE), corresponding to the oxygen reduction process. This characteristic peak was completely absent in the N₂-purged electrolyte, confirming the intrinsic ORR activity of the honeycomb carbon structure under acidic conditions. Complementary LSV measurements (Fig. S6b) further demonstrated superior electrocatalytic performance with a half-wave potential ($E_{1/2}$) of 0.572 V. These experimental results provide direct evidence that the atomic Co-N_x moieties embed-

ded in the carbon matrix serve as catalytically active centers, effectively facilitating the four-electron oxygen reduction pathway in acidic media.

Notably, the atomic Co-N_x moieties embedded in the carbon matrix do not directly serve as dominant catalytic sites under the high Pt loading conditions of Pt/HNC-400. Instead, they play a critical electronic modulation role: XPS analysis (Fig. 5) reveals a distinct negative shift in the Pt 4f binding energy, indicating electron transfer from the Co-N_x-doped carbon support to Pt nanoparticles. This strong metal-support interaction optimizes the d-band center of Pt, thereby enhancing its intrinsic ORR activity. The synergistic effect thus arises from the combination of (1) the high dispersion and small size of Pt nanoparticles facilitated by the hierarchical porous architecture, and (2) the electronic modulation imparted by the Co-N_x moieties, which together boost both activity and stability.

The durability of HNC-400 was rigorously evaluated through accelerated durability testing (ADT). After 10 000 electrochemical cycles, the cathodic peak potential shifted negatively by 78 mV (Fig. S6a), while the $E_{1/2}$ decreased by 52 mV (Fig. S6b). Notably, the quasi-rectangular CV profiles retained high capacitive behavior, indicating that the structural integrity of the honeycomb carbon framework was well preserved. This moderate degree of performance attenuation further underscores the exceptional stability afforded by the hierarchical porous architecture.

To elucidate the origin of performance degradation, hydrodynamic voltammetry was conducted at various rotation speeds (400-2500 r/min). As shown in

Fig. S6c, the diffusion-limited current densities exhibited a linear dependence on $\omega^{1/2}$ ($R^2 = 0.987$), consistent with the predictions of the Levich equation. Koutecký-Levich analysis (0.4–0.7 V vs. RHE) yielded electron transfer numbers (n) ranging from 3.12 to 3.58 across 4 independent measurements, with a weighted average of 3.37 ± 0.18 . This deviation from the ideal four-electron pathway ($n = 3.9$ – 4.0 for Pt/C) suggests the partial generation of peroxide ($n \approx 2$) during the ORR. The localized accumulation of reactive oxygen species, particularly $\bullet\text{OOH}$ intermediates from the two-electron pathway, likely induces oxidation of the carbon matrix and leaching of active sites.

The correlation between silica content and electrocatalytic performance was systematically investigated using CV in O_2 -saturated $0.1 \text{ mol L}^{-1} \text{ HClO}_4$. As shown in Fig. 6a, the electrochemically active surface area (ECSA) determined by hydrogen underpotential deposition revealed significant differences among the catalysts: Pt/HNC-400 exhibited the highest ECSA ($144.1 \text{ m}^2/\text{g}$), followed by Pt/HNC-700 ($93.8 \text{ m}^2/\text{g}$)

and Pt/HNC-100 ($81.9 \text{ m}^2/\text{g}$). Combining the calculated ECSA values with the BET surface area and SEM results, it can be inferred that the hierarchical porosity of HNC-400 enables high-density Pt nucleation, quantum confinement effects, and stabilized metal support interactions. As illustrated in the LSV curves of Fig. 6b, the half-wave potential of Pt/HNC-400 reaches 0.901 V , surpassing those of Pt/HNC-700 (0.894 V) and Pt/HNC-100 (0.885 V). Moreover, the limiting diffusion current density of Pt/HNC-400 is measured at $6.97 \text{ mA}/\text{cm}^2$, significantly higher than the values of $6.26 \text{ mA}/\text{cm}^2$ for Pt/HNC-700 and $5.67 \text{ mA}/\text{cm}^2$ for Pt/HNC-100. This disparity is attributed to the 3D interconnected porous structures of Pt/HNC-400 and Pt/HNC-700, which endow them with superior O_2 permeability, proton conductivity, and electron transfer capability.

To compare the intrinsic ORR activity of the three catalysts, their mass activity and specific activity were also calculated (Fig. 6c). The Pt/HNC-400 catalyst attains the highest mass activity of $1.84 \text{ A}/\text{mg}$,

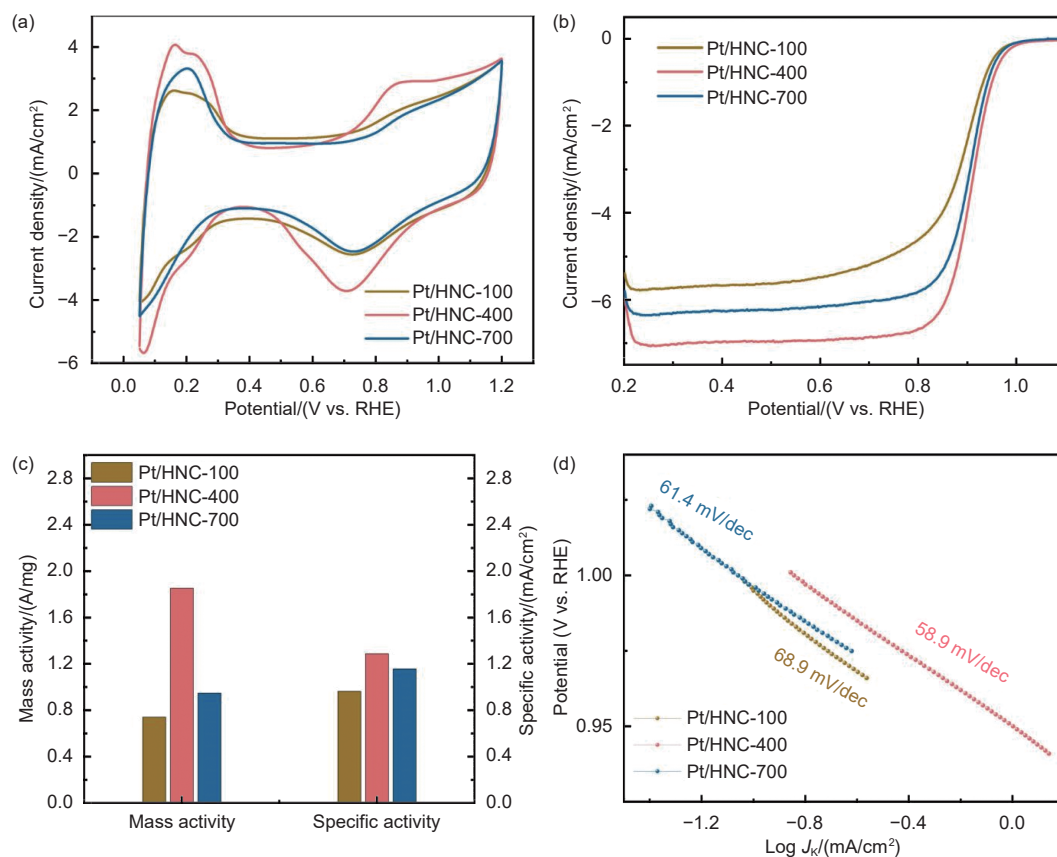


Fig. 6 (a) Cyclic voltammograms recorded in N_2 -saturated 0.1 mol/L HClO_4 at 50 mV/s for ECSA determination. (b) LSV curves in O_2 -saturated 0.1 mol/L HClO_4 at 10 mV/s and 1600 r/min . (c) Mass activity (MA) and specific activity (SA) at 0.9 V vs. RHE . (d) Tafel plots derived from LSV curves

outperforming Pt/HNC-100 (0.75 A/mg) and Pt/HNC-700 (0.94 A/mg). Additionally, the specific activity of Pt/HNC-400 is 1.29 mA/cm², higher than 0.96 mA/cm² for Pt/HNC-100 and 1.16 mA/cm² for Pt/HNC-700. Collectively, the electrochemical results indicate that the ORR catalytic performance of the 3 catalysts follows the order: Pt/HNC-400>Pt/HNC-700>Pt/HNC-100. This trend can be rationalized by the fact that the larger BET surface area of the HNC-400 support provides more anchoring sites for Pt nanoparticles. To analyze the kinetic behavior of the catalysts, Tafel plots were recorded and their slopes were calculated (Fig. 6d). The Pt/HNC-400 catalyst exhibits the lowest slope value of 58.8 mV/dec, compared to 68.9 mV/dec for Pt/HNC-100 and 61.4 mV/dec for Pt/HNC-700, indicating a faster kinetic process during the electrocatalytic ORR. This kinetic superiority is likely attributed to the optimized large-pore structure of the catalyst, which facilitates efficient mass transfer and reaction progression.

Fig. 7a illustrates the ADT results of three dis-

tinued Pt/HNC samples, each subjected to 10 000 cycles. The data obtained clearly demonstrate a gradual decrease in the hydrogen absorption area with increasing cycle number. It is a well-recognized principle that the reduction in electrochemically active surface area can be quantitatively evaluated by analyzing changes in the Pt-related hydrogen absorption area, providing a reliable method for assessing the loss of active sites on the catalyst surface. After the ADT test, the ECSA values of the Pt/HNC-100, Pt/HNC-400, and Pt/HNC-700 catalysts were precisely determined to be 65.9, 102.7 and 84.5 m²/g, respectively. Correspondingly, their ECSA retention rates were calculated as 80.4%, 71.4% and 89.7%, respectively. Notably, although Pt/HNC-400 exhibits the highest post-ADT ECSA among the three samples, its retention rate is the lowest. This seemingly paradoxical result can be reasonably attributed to the coexistence of competing degradation mechanisms, namely Pt nanoparticle detachment and carbon matrix corrosion. The hierarchical porous structure of HNC-

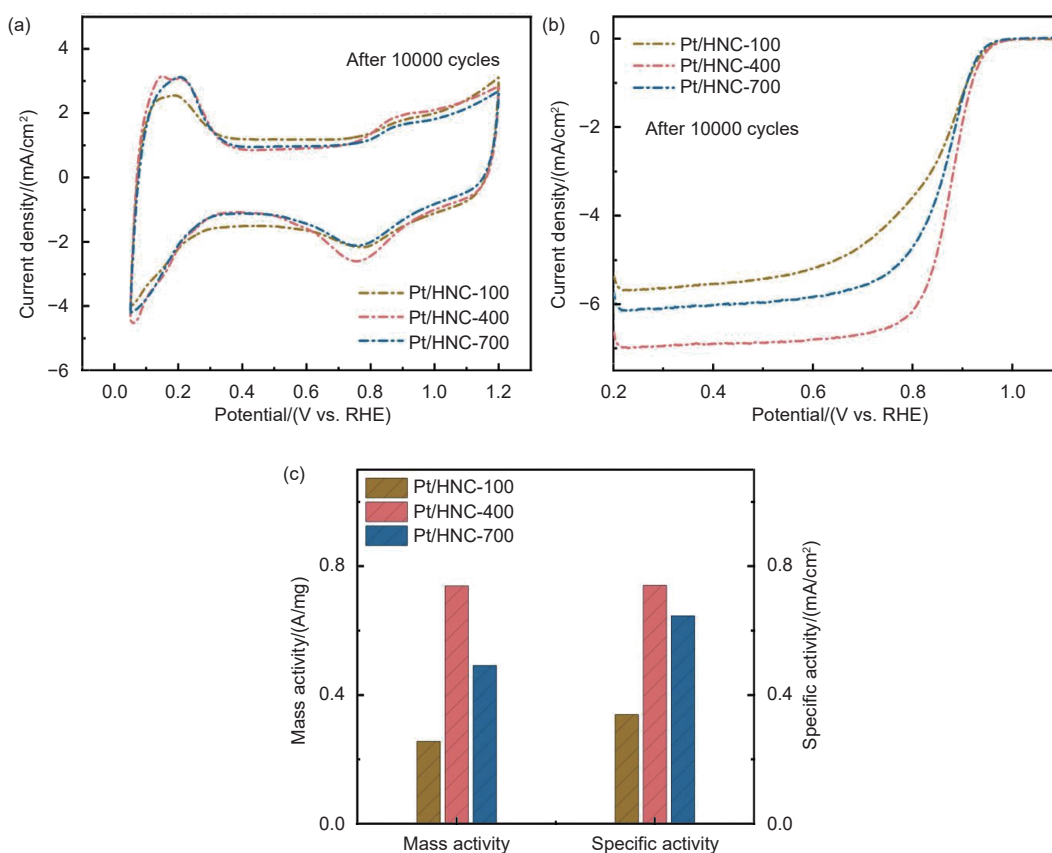


Fig. 7 (a) CV curves, (b) LSV curves, and (c) histograms of mass activity vs. specific activity for Pt/HNC catalysts prepared with different SiO₂ additions after ADT cycling

400, while facilitating excellent initial Pt dispersion, simultaneously increases the number of triple-phase boundaries. Such enhanced triple-phase boundaries can accelerate carbon oxidation during high-potential cycling, as previously reported for high-surface-area carbon supports where increased exposure to reactive species promotes corrosion^[30–31]. Consequently, despite its initially high ECSA, Pt/HNC-400 experiences a relatively lower retention rate, yet maintains the highest absolute ECSA post-ADT, underscoring its superior overall stability.

As shown in the LSV curves in Fig. 7b, the half-wave potentials of Pt/HNC-100, Pt/HNC-400 and Pt/HNC-700 decreased by 31, 25 and 30 mV, respectively, with corresponding reductions in limiting current densities of 0.13, 0.08 and 0.24 mA/cm². These results indicate that carbon corrosion of the HNC support occurred after ADT, triggering 2 parallel degradation mechanisms that collectively impair catalytic performance. Primarily, corrosion-induced damage to the carbon substrate integrity facilitates the detachment of Pt nanoparticles, leading to a decrease in the catalyst's ECSA a trend consistent with the ECSA retention data discussed earlier. Furthermore, carbon corrosion causes partial collapse of the 3D interconnected porous structure, which compromises the catalyst's electrical conductivity and mass transport properties. This dual degradation mechanism encompassing both active site loss and conductive network deterioration ultimately manifests as the observed declines in reaction kinetics (reflected by half-wave potential shifts) and mass transport efficiency (evidenced by limiting current density reductions).

To comprehensively assess changes in catalytic activity following ADT, the mass activity and specific activity of the three Pt/HNC catalysts were meticulously calculated. As illustrated in Fig. 7c, the specific activity retention rates of Pt/HNC-100, Pt/HNC-400 and Pt/HNC-700 were determined to be 35.2%, 55.3% and 55.7%, respectively. Notably, Pt/HNC-400 and Pt/HNC-700 characterized by their multi-dimensional porous structures exhibited significantly higher specific activity retention rates compared to Pt/HNC-100.

This result provides robust experimental evidence for the beneficial effect of such unique porous architectures in enhancing the overall stability of the catalysts. By integrating the analyses of ECSA retention, half-wave potential decay, and specific activity retention after ADT cycling, Pt/HNC-400 demonstrates superior ORR stability among the 3 investigated samples. This multi-faceted evaluation framework deepens the understanding of catalyst performance degradation mechanisms and serves as a critical basis for the rational design of high-stability electrocatalysts. The strong metal-support interaction in Pt/HNC-400 is confirmed through complementary evidence: XPS reveals electronic modulation (0.4 eV shift), TEM shows physical confinement within pore channels, and ADT demonstrates exceptional durability. This multi-faceted interaction effectively pins Pt nanoparticles to the carbon substrate, suppressing both detachment and ripening during electrochemical cycling.

To gain a more in-depth understanding of the structural advantages of HNC in the ORR, a control catalyst (Pt/CNC) was synthesized. The Pt/CNC catalyst was prepared by template-free pyrolysis of ZIF-67 dodecahedrons, followed by ethylene glycol-assisted Pt deposition (Fig. S2). SEM analysis of Pt/CNC reveals that it partially retains the polyhedral morphology of the ZIF-67 precursor, with surface roughening attributed to the in-situ formation of mesopores during carbonization. XRD pattern of Pt/CNC exhibits distinct characteristic peaks at 39.8°, 46.3°, 67.5° and 81.7°, which can be accurately indexed to the (111), (200), (220) and (311) planes of face-centered cubic Pt crystallites (PDF # 04-002-0887). Nitrogen physisorption measurements indicate that the CNC support has relatively limited porosity, with a BET surface area of 97.3 m²/g starkly contrasting with the hierarchical architecture of HNC-400, which exhibits a significantly higher BET surface area of 435.1 m²/g. Electrochemical evaluations further demonstrate that the Pt/HNC-400 catalyst possesses an exceptional electrochemically active surface area (ECSA) of 144.1 m²/g, outperforming both commercial Pt/C (66.2 m²/g) and the Pt/CNC catalyst (53.6

m²/g). This superior ECSA of Pt/HNC-400 stems from its unique 3D interconnected pore network, which simultaneously facilitates high-degree Pt dispersion, efficient mass transport of reactants and products, and unobstructed electron conduction. Such structural synergy effectively suppresses the coalescence of Pt nanoparticles during ORR operation, thereby offering a novel and promising paradigm for designing highly durable electrocatalysts through multiscale porosity engineering.

Fig. 8b illustrates the LSV curves of commercial Pt/C, Pt/CNC, and Pt/HNC-400 catalysts, recorded in an O₂-saturated 0.1 mol/L HClO₄ electrolyte at ambient temperature. The LSV results show that Pt/HNC-400 exhibits a $E_{1/2}$ of 0.901 V, which is 41 mV higher than that of commercial Pt/C. In sharp contrast, Pt/CNC displays the lowest $E_{1/2}$ at 0.837 V even inferior to those of Pt/HNC-100 (0.885 V) and Pt/HNC-700 (0.894 V) as previously reported. Additionally,

the limiting current densities of Pt/CNC and Pt/HNC-400 are determined to be 6.21 and 6.97 mA/cm², respectively, both surpassing that of commercial Pt/C (5.98 mA/cm²). These findings indicate that the carbon supports derived from HNC and ZIF-67 pyrolysis possess superior electrical conductivity compared to the carbon black in commercial Pt/C.

The mass activity and specific activity of the catalysts were further evaluated (Fig. 8c). Notably, Pt/HNC-400 achieves the highest performance metrics, with a MA of 1.84 A/mg and a SA of 1.29 mA/cm², significantly outperforming both Pt/CNC and commercial Pt/C. Tafel plots (Fig. 8d) were used to assess ORR reaction kinetics. Pt/HNC-400 exhibits the smallest Tafel slope of 58.8 mV/dec, compared to 80 mV/dec for commercial Pt/C and 78 mV/dec for Pt/CNC. This confirms that Pt/HNC-400 possesses the fastest ORR kinetics and optimal catalytic performance among all tested samples. It is important to note

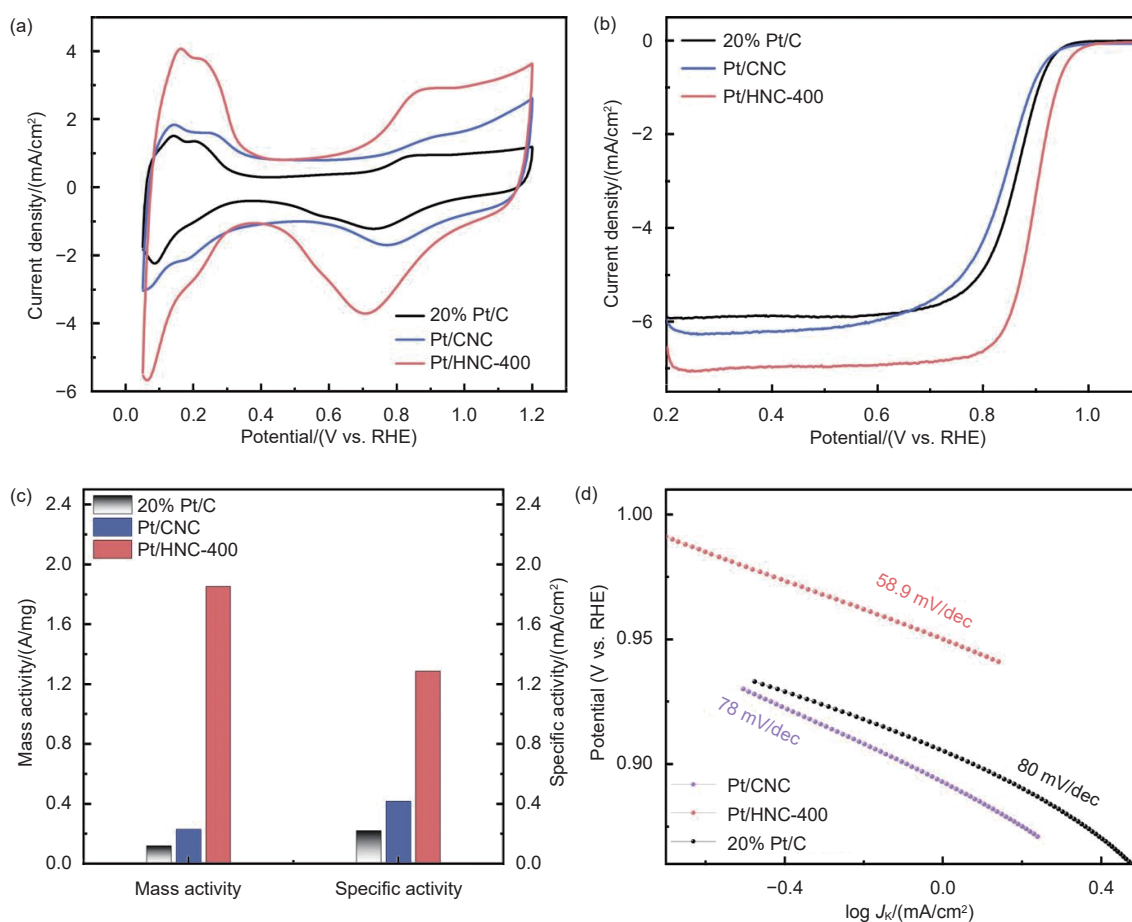


Fig. 8 (a) CV curves, (b) LSV curves, (c) Mass activity vs. specific activity histograms, and (d) Tafel curves for the Pt/CNC, Pt/HNC-400 and commercial Pt/C catalysts

that, given the high Pt loading (16.7%) and the well-established superior intrinsic ORR activity of Pt, the measured catalytic performance of Pt/HNC-400 is predominantly attributed to the Pt nanoparticles. The atomic Co-N_x moieties embedded in the carbon support do not serve as primary catalytic sites under these conditions; rather, they play a secondary but critical synergistic role by modulating the electronic structure of Pt by strong metal-support interactions, as evidenced by XPS binding energy shifts (Fig. 5). This electronic modulation optimizes the adsorption energetics of oxygen intermediates on Pt, thereby enhancing both activity and durability.

Collectively, these comprehensive electrochemical characterizations demonstrate that Pt/HNC-400 outperforms both Pt/CNC and commercial Pt/C in terms of ORR catalytic activity. Its superior performance stems from multiple synergistic factors: First, uniformly dispersed, small-sized Pt nanoparticles enhance the utilization efficiency of precious metals, maximizing the active surface area available for ORR. Second, the strong interaction between Pt nanoparticles and the honeycomb carbon matrix effectively boosts the intrinsic catalytic activity of Pt species. Third, the high-specific-surface-area, 3D multi-channel honeycomb architecture facilitates efficient mass transfer of reactants and products, reducing diffusion limitations and improving overall reaction rates. Fourth, Co-N_x functional groups in the honeycomb carbon matrix act as additional ORR active sites, further enhancing catalytic performance. These findings provide valuable insights into the design principles for developing high-efficiency ORR electrocatalysts.

The stability of the three catalysts was systematically investigated by ADT at a scan rate of 100 mV/s. Remarkably, even after 10 000 ADT cycles, the Pt/HNC-400 catalyst retained excellent catalytic activity, with all ORR performance parameters outperforming those of both Pt/CNC and commercial Pt/C. As illustrated in Fig. 9a, the electrochemically active surface area (ECSA) of Pt/HNC-400 remained at 102.7 m²/g post-ADT more than double that

of Pt/CNC (46.5 m²/g) and commercial Pt/C (41.7 m²/g). The LSV curves depicted in Fig. 9b further highlight the superior stability of Pt/HNC-400, with a $E_{1/2}$ decay of only 25 mV significantly lower than the 80 mV decay of commercial Pt/C and 58 mV decay of Pt/CNC. The Co-N_x moieties not only contribute catalytically but also modulate the electronic structure of Pt nanoparticles through metal-support interaction, as evidenced by the Pt 4f peak shift (Fig. 5b). This synergistic effect between Co-N_x sites and Pt nanoparticles creates optimized electrocatalytic micro-regions that enhance both activity and durability.

A comparative analysis of mass activity and specific activity after ADT (Fig. 9c), further confirms the exceptional stability of Pt/HNC-400. Its specific activity retention rate was determined to be 55.3%, substantially higher than those of Pt/CNC (15.2%) and commercial Pt/C (14.8%). Collectively, these comprehensive experimental results provide conclusive evidence for the outstanding long-term stability of the Pt/HNC-400 catalyst, underscoring its potential as a promising candidate for practical applications in electrochemical devices requiring high-performance, durable ORR electrocatalysts.

To provide additional conclusive evidence for the outstanding stability of the Pt/HNC-400 catalyst, the time-current (i-t) chronoamperometry technique was employed to evaluate its current retention performance over an extended period of 50 000 s. As clearly depicted in Fig. 10a, the Pt/HNC-400 catalyst exhibited an impressive current retention rate of 80%, significantly higher than that of commercial Pt/C (67%). This result further confirms the superior durability of Pt/HNC-400 under continuous ORR operation conditions. In the context of ORR, the four-electron reaction pathway is widely recognized as the most efficient route for achieving high-performance electrocatalysis.

To elucidate the ORR reaction mechanism of the Pt/HNC-400 catalyst, LSV curves at different rotational speeds were acquired (Fig. 10b). Based on the relationship between rotational speed and limiting cur-

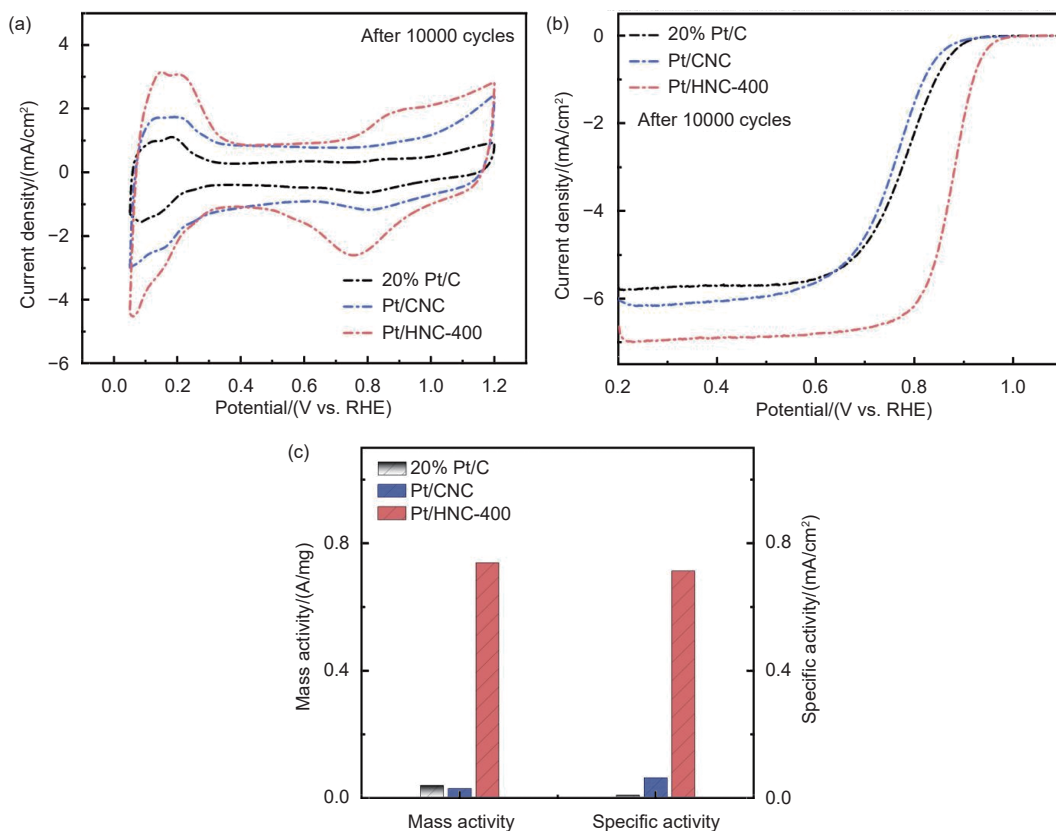


Fig. 9 (a) CV curves, (b) LSV curves, and (c) mass activity vs. specific activity histograms for Pt/CNC, Pt/HNC-400 and commercial Pt/C catalysts after ADT testing

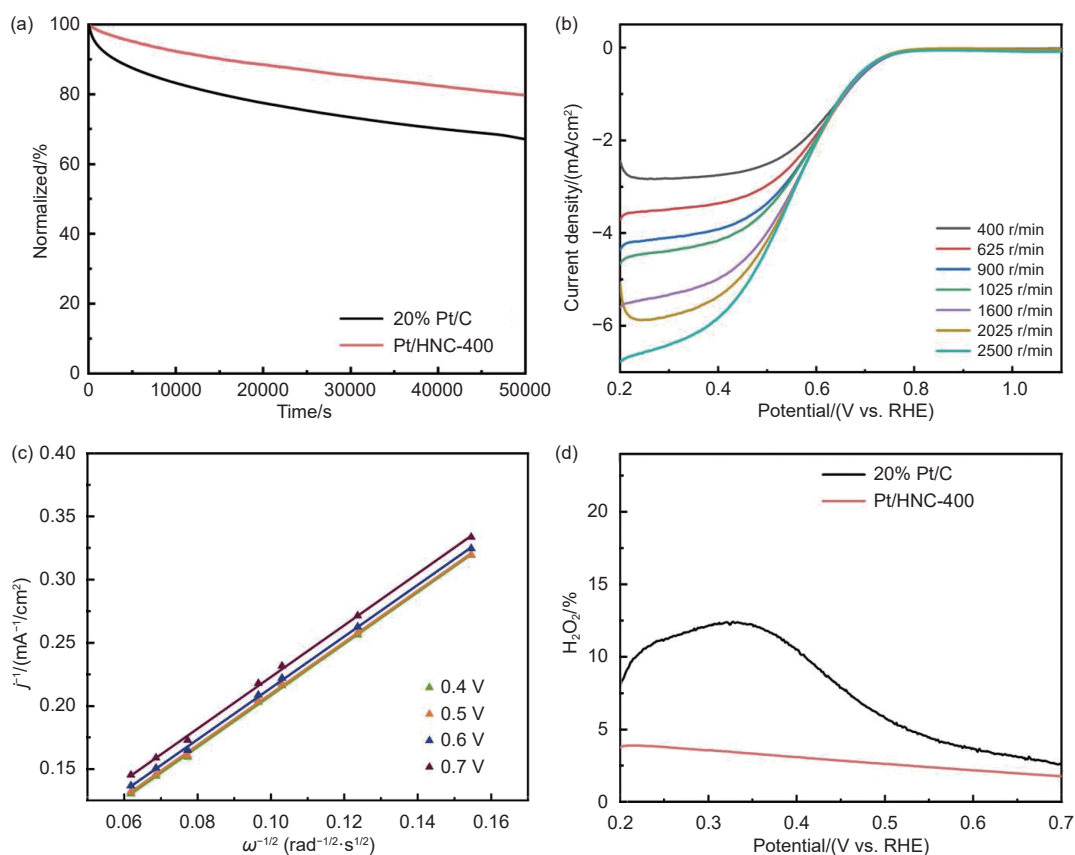


Fig. 10 (a) i-t curves and (b) LSV curves for Pt/HNC-400 catalyst at different rotational speeds. (c) K-L curves. (d) H_2O_2 yields for RRDE tests

rent described by the Koutecky-Levich (K-L) equation, K-L curves were constructed for various applied potentials. As illustrated in Fig. 10c, the slopes of the K-L lines remained remarkably consistent within the potential range of 0.4-0.7 V (vs. RHE). Detailed analysis yielded an estimated electron transfer number (n) of 3.94 for Pt/HNC-400, strongly indicating that the ORR process on its surface predominantly follows a four-electron reaction pathway.

To further confirm this mechanism, the H_2O_2 yield of Pt/HNC-400 was measured using a RRDE. As shown in Fig. 10d, the calculated electron transfer number (n) values ranged from 3.7 to 3.9, which are in excellent agreement with the results derived from the K-L plots. Additionally, the H_2O_2 yield of Pt/HNC-400 was found to be less than 5% within the potential range of 0.2-0.8 V (vs. RHE), significantly lower than that of commercial Pt/C. Collectively, these comprehensive experimental results demonstrate that the ORR process on Pt/HNC-400 follows a highly efficient four-electron pathway, minimizing the formation of undesirable byproducts. This characteristic is crucial for enhancing the overall performance and energy efficiency of electrochemical devices, underscoring the great potential of Pt/HNC-400 as an advanced ORR electrocatalyst. Benchmarking against recent literature reveals (Table 2) that Pt/HNC-400 achieves one of the highest mass activities reported for Pt-based ORR catalysts (1.84 A/mg), significantly exceeding the DOE 2020 target (0.44 A/mg)^[32–36]. While ordered intermetallic structures offer superior long-term stability, our catalyst demonstrates that hierarchical porous carbon engineering combined with atomic Co-N_x sites provides an effective strategy for simultaneously achieving high activity and good durability, representing a promising direction for practical fuel cell applications.

To provide a deeper mechanistic understanding of the observed structure-performance correlations, we have integrated our multi-dimensional characterization data to offer explicit evidence addressing the key points raised. First, regarding the oxidation of the carbon matrix and leaching of active sites, while direct detection of solvated Pt ions or gaseous CO_2 is challenging, our electrochemical data provide strong corroborating evidence. The decrease in limiting current density for all Pt/HNC catalysts after ADT (a reduction of 0.13, 0.08 and 0.24 mA/cm² for Pt/HNC-100, Pt/HNC-400 and Pt/HNC-700, respectively (Fig. 7b)) serves as a sensitive indicator of increased mass transport resistance. This degradation in mass transport directly points to the corrosion and collapse of the porous carbon structure, a hallmark of carbon oxidation. Concomitantly, the loss of electrochemically active surface area (e.g., for Pt/HNC-400, 144.1-102.7 m²/g) quantitatively reflects the reduction in Pt active sites. This reduction is a combined result of Pt nanoparticle detachment (caused by carbon corrosion) and/or Ostwald ripening, with the detachment process itself constituting the leaching of active sites from the electrode. Second, the relationship between carbon oxidation and a lower ECSA retention rate is, in fact, central to our discussion. Pt/HNC-400 possesses the highest initial ECSA (144.1 m²/g) and the largest BET surface area (435.1 m²/g), yet its ECSA retention (71.4%) is lower than that of Pt/HNC-700 (89.7%). This seemingly paradoxical result is direct evidence of the trade-off inherent in its unique structural advantages. As argued in the manuscript, the hierarchical porous structure of HNC-400, while providing excellent initial dispersion and anchoring for Pt nanoparticles, also creates a more extensive network of triple-phase boundaries. These boundaries are not only the crucial sites for electrochemical reactions but also the most vulnerable regions to carbon corrosion

Table 2 Comparison of ORR performance for Pt/HNC-400 with recently reported high-performance electrocatalysts

Catalyst	Electrolyte	$E_{1/2}$ (V vs. RHE)	Mass activity@0.9 V/(A/mg)	Durability (ECSA retention)	Ref.
Pt/HNC-400	0.1 mol/L HClO_4	0.90	1.84	71% after 1×10^4 cycles	This work
o-PtCo@CoNC	0.1 mol/L HClO_4	~ 0.92	1.21	~ 90% after 5×10^4 cycles	[32]
Pt/Fe ₂ P@CoP@NDC	0.5 mol/L H_2SO_4	~ 0.87	0.96	$5.77 \times$ Pt/C after 1000 cycles	[33]
PtP _{1.4} @Pt/C	0.1 mol/L HClO_4	~ 0.91	0.31	94% after 3×10^4 cycles	[34]
PtCoCu with Iodine	0.1 mol/L HClO_4	~ 0.93	0.53	94% after 3×10^4 cycles	[35]
Commercial Pt/C	0.1 mol/L HClO_4	0.84	0.12	46% after 3×10^4 cycles	[36]

under high-potential cycling. Therefore, the more abundant triple-phase boundaries, while responsible for the high initial activity, also lead to a faster rate of interfacial carbon oxidation. A direct consequence of this carbon oxidation is the loss of anchoring points for Pt nanoparticles, triggering more significant Pt detachment and ultimately manifesting as a relatively lower ECSA retention rate. This interpretation perfectly links the structural features (high surface area, porosity) with the electrochemical outcome (ECSA retention). Third, concerning the dual degradation mechanism, our evidence is equally clear. This mechanism comprises 2 parallel and interconnected processes: (1) Active site loss: Pt nanoparticle detachment, induced by carbon corrosion, directly leads to a decrease in ECSA. (2) Deterioration of the conductive network and mass transport pathways: The partial collapse of the 3D framework due to corrosion disrupts the continuity for electron conduction and blocks the diffusion channels for reactants and products. The combined effect of these two processes is ultimately reflected in the macroscopic electrochemical performance through two key metrics: sluggish reaction kinetics (indicated by the negative shift in half-wave potential, $E_{1/2}$, with Pt/HNC-400 decaying only 25 mV compared to 80 mV for Pt/C) and reduced mass transport efficiency (evidenced by the decrease in limiting current density). Thus, by monitoring both the $E_{1/2}$ shift and the change in limiting current density, we can comprehensively track the impact of the dual degradation mechanism on catalyst performance. Finally, regarding the role of multi-dimensional porous structures in higher activity retention, our analysis indicates that their function is not simply to achieve a higher ECSA retention, but rather to preserve a high intrinsic activity of the sites that remain after degradation. This is most clearly demonstrated by the specific activity retention rate. Although Pt/HNC-400 does not have the highest ECSA retention, its specific activity retention (55.3%) is comparable to that of Pt/HNC-700 (55.7%) and significantly exceeds that of Pt/HNC-100 (35.2%, Fig. 7c). Specific activity, which normalizes performance to ECSA, is a measure of the intrinsic catalytic capability of the active sites. The excellent specific activity retention of Pt/HNC-400 and Pt/HNC-700 provides

direct proof that their multi-dimensional pore structures can: (1) physically confine Pt nanoparticles, inhibiting their migration and agglomeration during potential cycling; and (2) synergize with Co-N_x moieties to stabilize the electronic structure of Pt through strong metal-support interactions. This electronic stabilization ensures that, even after partial carbon corrosion occurs, the remaining Pt sites can still catalyze the ORR efficiently. Therefore, the “higher activity retention” is a manifestation of both “structural robustness” and “electronic stability” synergistically conferred by the multi-dimensional porous architecture.

4 Conclusion

In this study, a honeycomb carbon-supported Pt catalyst (Pt/HNC) with a 3D cross-linked hierarchical pore structure was successfully synthesized by a synergistic strategy combining template-assisted pyrolysis and alcohol reduction. The as-prepared Pt/HNC-400 exhibits superior ORR performance compared to commercial Pt/C: its half-wave potential is 41 mV higher, mass activity is 15.3 times greater, and after 10 000 accelerated durability test cycles, its half-wave potential decays by only 25 mV (vs. 80 mV for Pt/C) with higher ECSA retention. The exceptional performance stems from the synergistic effects of multiple factors: small Pt nanoparticles enhance utilization efficiency; strong metal-support interaction boosts intrinsic catalytic activity; the 3D hierarchical pore structure improves mass transfer efficiency and exposes more active sites; and in-situ formed Co-N_x groups provide additional catalytic active sites. This facile synthesis strategy addresses the inherent limitations of conventional carbon supports, offering a promising approach for fabricating high-specific-surface-area porous catalysts for advanced electrochemical devices.

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