

Nitrogen functionalized metal-free catalysts enabling active hydrogen-mediated pathway toward efficient H₂O₂ electro-synthesis

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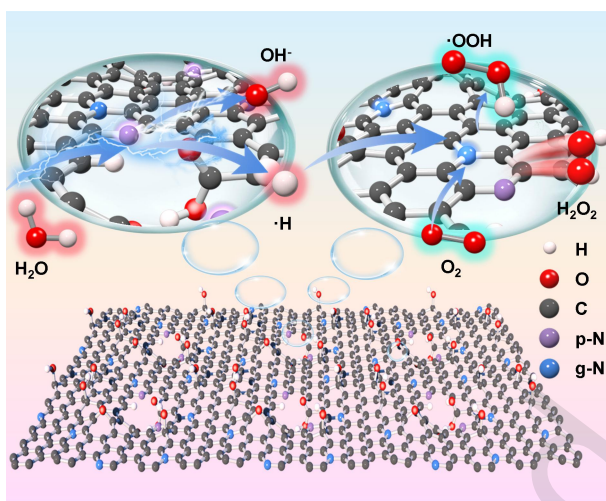
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The generation of active hydrogen over metal-free catalyst is achieving, thereby regulating hydrogenation pathway of O_2 and facilitating H_2O_2 electrosynthesis through nitrogen functionalization in a carbon matrix.

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ABSTRACT: The electrosynthesis of H₂O₂ via the two-electron oxygen reduction reaction represents a promising alternative to the anthraquinone oxidation process. However, concurrently achieving high Faradaic efficiency (FE) and industrial-level productivity remains challenging, largely due to the intrinsically sluggish kinetics of proton-coupled electron transfer (PCET). Herein, we first report the generation of active hydrogen (•H) over metal-free catalyst, thereby regulating hydrogenation pathway and facilitating H₂O₂ electrosynthesis through nitrogen functionalization in a carbon matrix. In situ characterizations and theoretical calculations reveal a dual-site synergistic mechanism in which pyridinic N sites facilitate H₂O dissociation to generate •H species, while graphitic N sites electronically activate adjacent carbon atoms, facilitating efficient O₂ adsorption and activation. The generated •H subsequently participate in the •O₂-to-•OOH reaction, thus bypassing the •O₂ intermediate and lowering the free energy effectively. As a result, the optimized metal-free carbon catalyst, delivers a high FE of 96.4% with productivity of 14.3 mol/g/h at a current density of ~400 mA/cm² in flow cell, outperforming the counterpart governed by a PCET-mediated pathway. This work demonstrates that metal-free active site can promote •H generation and regulate hydrogenation pathways, thereby enhancing O₂-to-H₂O₂ conversion.

KEYWORDS: H₂O₂ production, 2e⁻ ORR, metal-free catalysts, active hydrogen generation, active hydrogen transfer.

1. Introduction

Hydrogen peroxide (H₂O₂) is an essential oxidant for water treatment, chemical synthesis, and disinfection, yet its industrial production relies on the energy-intensive and centralized anthraquinone process (AOP). Electrochemical oxygen reduction via the two-electron pathway offers a sustainable alternative for on-site H₂O₂ generation, but its application is constrained by the intrinsic trade-off between activity and selectivity dictated by scaling relationships among •O₂, •OOH, and •O intermediates [1-6]. In conventional proton-coupled electron transfer (PCET) pathway (**Fig. 1(a)**), O₂ is first adsorbed and activated on catalytic sites, followed by sequential proton-electron

coupling to generate the •OOH intermediates (O₂ → •O₂⁻ → •OOH) [7-9]. However, this process is intrinsically limited by the high energy barrier associated with H₂O dissociation or the sluggish kinetics of proton transfer, particularly in alkaline media, which often leads to insufficient proton supply [10]. In contrast, the active hydrogen (•H) transfer (AHT) pathway provides an alternative hydrogenation mechanism that bypasses sequential proton-electron delivery [11]. In this process, reactive •H species participate in O₂ activation thus •OOH formation from O₂ only by one step (O₂ → •OOH), enabling more efficient hydrogenation kinetics (as shown in **Scheme 1**) [12]. Notably, the generation of •H via H₂O dissociation has been predominantly observed on metal-based active sites in

previous studies because of their favorable water dissociation capability [12-14]. However, these metal-based catalysts are generally susceptible to aggregation or

dissolution into the electrolyte (**Fig. 1(b)**), leading to poor operational stability at high current densities and possible metal contamination of the H_2O_2 product.

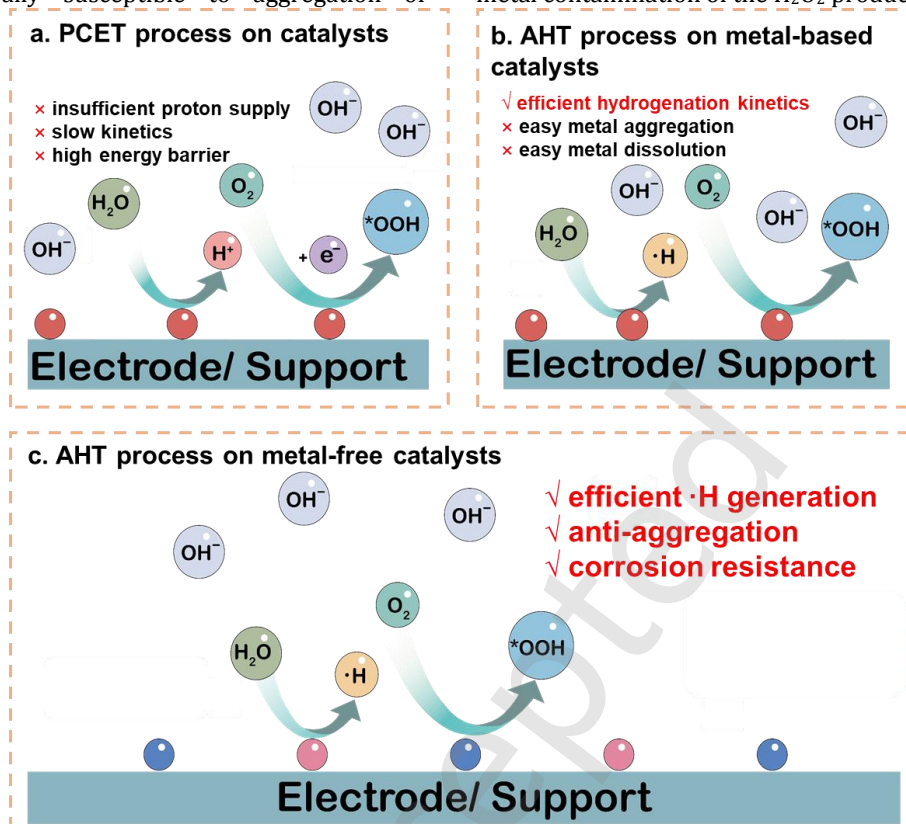
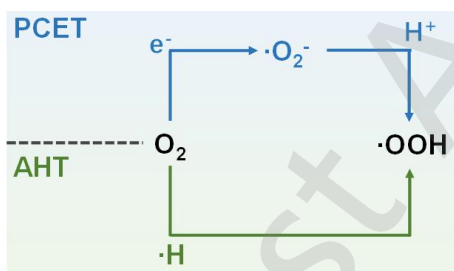


Fig. 1. Electrocatalytic O_2 -to- H_2O_2 reaction via different hydrogenation pathways. Schematic illustration of electrocatalytic O_2 -to- H_2O_2 reaction via (a) proton-coupled electron transfer (PCET) process on catalyst, (b) active hydrogen transfer (AHT) process on metal-based catalyst and (c) AHT process on metal-free catalyst in this work.



Scheme 1. Comparison of O_2 -to- H_2O_2 reaction via PCET process and AHT process.

In this context, heteroatom-doped metal-free carbon nanomaterials have emerged as promising electrocatalysts for the two-electron oxygen reduction reaction (2e^- ORR) toward H_2O_2 production owing to their tunable electronic structure, corrosion resistance, and anti-aggregation [15-18]. In particular, nitrogen functionalized carbon such as graphitic N, pyridinic N and pyrrolic N in carbon materials play key roles in modulating the charge density of adjacent carbon atoms and steering the reaction pathway between 2e^- pathway toward H_2O_2 and 4e^- pathway toward H_2O [15,18]. For example, graphitic N in carbon materials enables selective O_2 activation while suppressing the four-electron pathway, thereby providing a viable platform for sustainable H_2O_2 electrosynthesis [19]. On the other hand, pyrrolic N was also been identified as an active site for O_2 adsorption and activation in the 2e^- ORR [17]. Obviously, the nature of the active sites and the underlying catalytic mechanisms in

nitrogen-doped carbon materials remain debated. More importantly, the formation of $\cdot\text{H}$ species and the subsequent hydrogenation process on metal-free active sites during H_2O_2 electrosynthesis remain largely unexplored, likely due to the unfavorable H_2O dissociation kinetics on metal-free catalysts. Consequently, exploiting the active hydrogen transfer (AHT) pathway to enhance catalytic activity has been largely neglected in metal-free systems. Therefore, developing advanced metal-free electrocatalysts that enable efficient $\cdot\text{H}$ generation and elucidate the AHT mechanism would constitute an important breakthrough in H_2O_2 electrosynthesis.

Herein, we report a promising strategy for nitrogen-species functionalized metal-free electrocatalysts, featuring graphitic and pyridinic N sites, to enable efficient electrocatalytic O_2 reduction into H_2O_2 via AHT process. The experimental and DFT calculation results reveal a dual-site synergistic mechanism in which pyridinic N sites are beneficial to H_2O dissociation for the production of $\cdot\text{H}$, while graphitic N sites electronically activate adjacent carbon atoms, facilitating efficient O_2 adsorption and activation. The generated $\cdot\text{H}$ participates in O_2 reduction (**Fig. 1(c)**), lowering the free energy for O_2 activation and the formation of $\cdot\text{OOH}$ intermediate, thereby making H_2O_2 formation thermodynamically more favourable. The as-developed metal-free carbon electrocatalysts display remarkable 2e^- ORR performance, achieving high H_2O_2 FE and yield of 96.4% and 14.3 mol/g/h at high current density of $\sim 400 \text{ mA/cm}^2$

via kinetics-favourable AHT process, markedly surpassing the C₆₀₀ sample (47.8% and 5.54 mol/g/h at current density of ~150 mA/cm²) via PCET process.

2. Results and discussion

2.1 Structural characteristics

A series of N-doped carbon samples prepared at different pyrolysis temperatures and C₆₀₀ sample (no N-doping sample) were synthesized by conventional mixture pyrolysis method, as illustrated in Fig. S1 in the Electronic Supplementary Material (ESM). Notably, the pyridinic N to graphitic N ratio (p-N: g-N) is tunable by varying the pyrolysis temperature from 500 to 750°C (Fig. 2(a)). Transmission electron microscopy (TEM) is employed to characterize the nanostructures of N-C and C₆₀₀ samples. As shown in Fig. S2(a) in the ESM, the N-C₆₀₀ sample exhibits

well-defined, stacked multilayer nanosheets, confirming its highly lamellar and graphitic architecture. There are no obvious differences in the layering of the graphite in C₆₀₀, N-C₅₀₀, N-C₇₀₀ and N-C₇₅₀ (Figs. S2(b)-2(e) in the ESM), indicating that the N-doping and pyrolysis temperature have little influence on graphitic architecture. The high-resolution transmission electron microscopy (HRTEM) further reveals the detailed morphology of N-C and C₆₀₀ samples. As shown in Fig. S3(a) in the ESM, structure of N-C₆₀₀ exhibits ordered features, with evident short-range ordered graphite layers, which is almost same to C₆₀₀ and the other N-C samples (Figs. S3(b)-3(e) in the ESM) [20]. Elemental mapping using energy-dispersive X-ray spectroscopy (EDS, Fig. S4(a) in the ESM) confirms the homogeneous distribution of N, O and O across graphitic architecture, whereas no signal of N is detected in C₆₀₀ sample (Figs. S4(b) and S5 in the ESM).

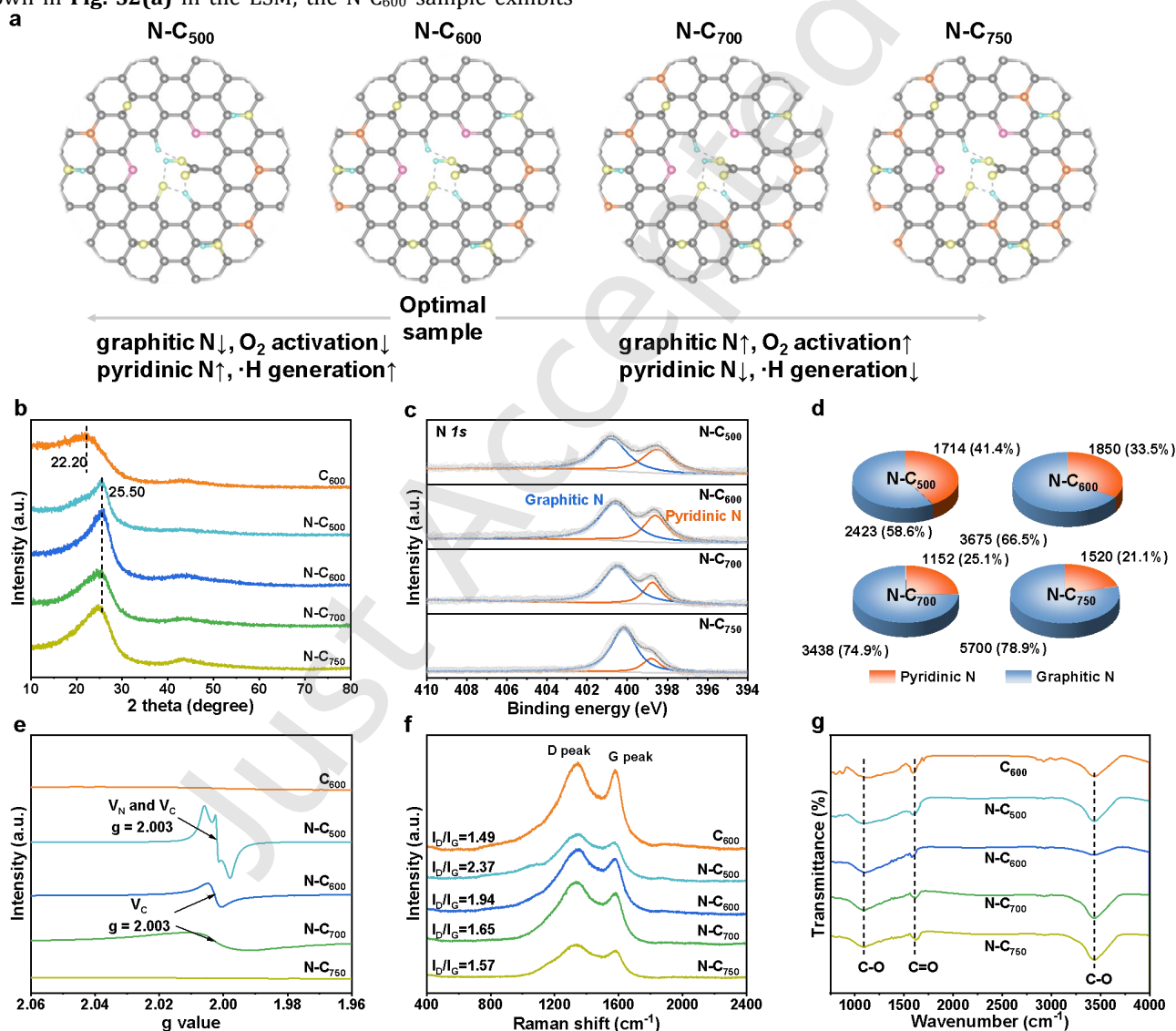


Fig. 2. Morphological and structural characterization. (a) Schematic diagram and model of the N-C samples preparation pathway (gray ball: carbon, orange ball: graphitic N, pink ball: pyridinic N, yellow ball: oxygen and blue ball: hydrogen). (b) XRD pattern of C₆₀₀, N-C₅₀₀, N-C₆₀₀, N-C₇₀₀ and N-C₇₅₀ samples. (c) High-resolution XPS spectra at N 1s level of N-C₅₀₀, N-C₆₀₀, N-C₇₀₀ and N-C₇₅₀ samples. (d) Relative percentages of the graphitic N and pyridinic N derived from the N 1s XPS spectrum. (e) EPR spectra, (f) Raman spectra and (g) FT-IR spectra of C₆₀₀, N-C₅₀₀, N-C₆₀₀, N-C₇₀₀ and N-C₇₅₀ samples.

The X-ray diffraction (XRD) pattern reveals characteristic peaks of all samples. As shown in Fig. 2(b), a broad peak at 22.20° is observed, which corresponds to the (002)

plane of graphite, indicating high graphitic degree [21]. Notably, significant shifts of the main diffraction peak toward higher angle are observed (22.20°→25.50°) in all N-

doping samples. The main diffraction peak shifts gradually with the N-doping amount increasing (**Fig. S6** in the ESM), suggesting the successful incorporation of N into graphitic lattice [22-24]. X-ray photoelectron spectroscopy (XPS) is further conducted to study the surface chemical composition. As shown in **Fig. S7** in the ESM, the XPS survey spectra of all the N-C samples deliver typical C 1s, N 1s, O 1s signals, while no N 1s signal is detected in that of C₆₀₀ sample. The accurate element contents of all the N-C and C₆₀₀ samples measured by XPS are given in **Table S1** in the ESM. Notably, the N element contents of all the N-C samples are almost same (6.09-7.57%), indicating that the pyrolysis temperature has little impact on the N-doping amount.

The high-resolution XPS spectra of all the N-C and C₆₀₀ samples is further conducted to identify the binding mode of N, C and O atoms in the material. As shown in **Fig. 2(c)**, the N 1s XPS spectrum can be deconvoluted into two peaks at 398.6 and 400.6 eV, which are assigned to pyridinic N and graphitic N, respectively [25-27]. The relative percentages of pyridinic N and graphitic N derived from the N 1s XPS spectrum of each sample are plotted in **Fig. 2(d)**. The pyridinic N percentages of total nitrogen for N-C₅₀₀, N-C₆₀₀, N-C₇₀₀ and N-C₇₅₀ samples are 41.4, 33.5, 25.1 and 21.1%, respectively. Notably, the pyridinic N percentage of total nitrogen decreases gradually with the increasing of pyrolysis temperature. It suggests that pyridinic N is easier to form than graphitic N at the low temperature (<600°C), while graphitic N is more stable at the high temperature (>700°C) [28]. The high-resolution C 1s XPS spectra of C₆₀₀ sample (**Fig. S8(a)** in the ESM) is deconvoluted into graphitic carbon (C-C) at 284.7 eV, C=N/C-O at 286.4 eV, C=O at 287.8 eV and O-C=O at 289.3 eV [25]. Compared to that of C₆₀₀ sample, all the N-C samples (**Figs. S8(b)-8(e)** in the ESM) exhibit an additional peak at 285.3 eV, corresponding to defective carbon [29]. With the increasing of pyrolysis temperature, the peak of defective carbon decreases gradually, probably owing to the decrease of pyridinic N content. The O 1s spectra of C₆₀₀ sample and all the N-C samples (**Figs. S9(a)-9(e)** in the ESM) can be deconvoluted into three peaks, corresponding to C=O (531.3 eV), C-O (532.3 eV) and COOH (533.5 eV) [23,30], indicating that the pyrolysis temperature has little effect on oxygen functional groups.

Electron paramagnetic resonance (EPR) is used to track the vacancies on the surface of graphitic architecture. As shown in **Fig. 2(e)**, the N-C₅₀₀ sample exhibits two distinct signals at $g = 2.003$, corresponding to nitrogen and carbon vacancies [31]. It is a direct consequence of the high pyridinic N content. In contrast, samples such as N-C₆₀₀ and N-C₇₀₀ exhibit a single EPR resonance signal, which can be attributed to carbon vacancies, likely due to their lower pyridinic N content compared to the N-C₅₀₀ sample. Vertically expanded EPR spectra of C₆₀₀ and N-C₇₅₀ samples are shown in **Fig. S10** in the ESM, indicating low carbon vacancy content. With the pyrolysis temperature increasing, the EPR resonance signal decrease significantly, indicating that the defect density is created by N-doping and relative with the contents of both pyridinic N and graphitic N. Raman spectroscopy is used to analyze the graphitization degree and defects in different N-C and C₆₀₀ samples. As shown in **Fig. 2(f)**, two strong peaks are observed at 1346 and 1583

cm⁻¹, corresponding to the D and G peaks, respectively [32]. The D and G peak corresponds to the defects in the carbon lattice and the stretching vibration of *sp*² C-C bonds, respectively, and the degree of defects in carbon materials is quantified by the intensity ratio of the D and G peaks (*I*_D/*I*_G) [33]. The *I*_D/*I*_G ratios of C₆₀₀ is 1.57, much smaller than that of different N-C samples, indicating that N-C samples have more defects owing to the N doping. The *I*_D/*I*_G ratios of different N-C decreases gradually with the pyrolysis temperature increasing, consistent with the pyridinic N content decreasing. Fourier-transform infrared spectroscopy (FT-IR) is also employed to study the surface properties of these samples. As shown in **Fig. 2(g)**, it is detected that the similar signals for C-O (1094, 3034 cm⁻¹) and C=O (1584 cm⁻¹) functional groups in C₆₀₀ and all the N-C samples, indicating that the N-doping into graphitic lattice has little influence on surface functional groups [34]. In all, all the structural characterization results reveal that nitrogen is incorporated into graphitic carbon in the form of graphitic N and pyridinic N, while oxygen is decorated on surface in the form of hydroxyl, carboxyl and carbonyl groups.

2.2 Electrocatalytic ORR performance

The electrocatalytic performance of samples for 2e⁻ ORR is evaluated in the H-cell with 1.0 mol/L KOH aqueous electrolyte. Cyclic voltammetry (CV) curves of C₆₀₀ and all the N-C samples at Ar and O₂ atmosphere are performed, respectively. As shown in **Fig. S11a**, the CV curve of C₆₀₀ at O₂ atmosphere displays a distinct ORR current at approximately 0.5 V vs. reversible hydrogen electrode (RHE) compared to that at Ar atmosphere, indicating its capability for catalyzing ORR. CV curves of all N-C samples are similar but show much higher current densities than that of C₆₀₀ (**Figs. S11(b)-11(e)** in the ESM). Comparing the CV curves of C₆₀₀ and all the N-C samples performed at O₂ atmosphere (**Fig. S11(f)** in the ESM), the current densities decrease gradually with the sample pyrolysis temperature increasing (from 500 to 750°C), indicating the great capability of graphitic N for O₂ activation. Linear sweep voltammetry (LSV) is then conducted to further quantify the ORR activity and similar results to CV curves are gained (**Fig. S12** in the ESM). Electrochemical impedance spectroscopy (EIS) is also performed (**Fig. S13** in the ESM). The Nyquist plots show gradually smaller arc radii with pyrolysis temperature increasing, indicating the higher interfacial charge transfer that attributable to the improved electrical conductivity and enhanced charge transfer kinetics. This is owing to the higher content of conductive graphitic N with pyrolysis temperature increasing, also promoting more effective ORR performance. In addition, electrochemically active surface area (ECSA) of C₆₀₀ and all the N-C samples is also assessed (**Figs. S14(a)-S14(e)** in the ESM). The C₆₀₀ sample shows the lowest ECSA, suggesting the importance of N-doping on specific surface area. The ECSA increases gradually with increasing pyridinic N content, owing to the carbon defects introduced by pyridinic N (**Fig. S14(f)** in the ESM). In all, electrocatalytic characterization results indicate that graphitic N improves electrical conductivity and enhances charge transfer kinetics to promote O₂ activation, while pyridinic N introduces carbon defects to increase ECSA.

LSV is then conducted on a rotating ring-disk electrode (RRDE) to further evaluate the $2e^-$ ORR performance of C_{600} and $N-C_{600}$. It shows that $N-C_{600}$ sample exhibits much higher ring current and smaller disk current than C_{600} sample (Fig. 3(a)), suggesting its preference for the $2e^-$ ORR pathway. The H_2O_2 selectivity and electron transfer number of the samples are plotted against the testing potential (Fig. 3(b)). Notably, $N-C_{600}$ demonstrates H_2O_2 Faradaic efficiency (FE) of around 99.0%, corresponding to an electron transfer number of approximately 2.02 at 0.6 V. Additionally, $N-C_{600}$ sample achieves a disk current density of 1.60 mA/cm^2 at 0.6 V, close to the equilibrium potential for $2e^-$ ORR, indicating efficient ORR kinetics with minimal overpotential for O_2 -to- H_2O_2 con-version [34].

Subsequently, the electrocatalytic performance of the samples for the $2e^-$ ORR toward H_2O_2 production was evaluated in 1.0 mol/L KOH using a flow cell equipped with a

polytetrafluoroethylene (PTFE)-treated carbon fiber paper gas diffusion electrode (GDE) using current-time (i-t) curve (from -0.1 to -0.5 V vs. RHE). The current densities also increase significantly (from ~ 150 to $\sim 400 \text{ mA/cm}^2$ at -0.4 V vs. RHE) after N-doping (Figs. 3(c) and S15 in the ESM), consistent with above results. The resulting H_2O_2 concentrations were quantified *via* Ce^{4+} titration and UV-vis spectrophotometry [26]. As shown in Figs. 3(d) and 3(e), the H_2O_2 yields of both $N-C_{600}$ and C_{600} samples under O_2 atmosphere increase linearly with a more negative applied potential, while their FE of H_2O_2 first increase and then decrease slightly. At -0.4 V vs. RHE , both C_{600} and $N-C_{600}$ achieve their highest FE. After N-doping into C_{600} , both the H_2O_2 FE and yield increase significantly (from 47.8% and 5.54 mol/g/h to 96.4% and 14.3 mol/g/h), indicating a significant effect of N-doping on ORR performance.

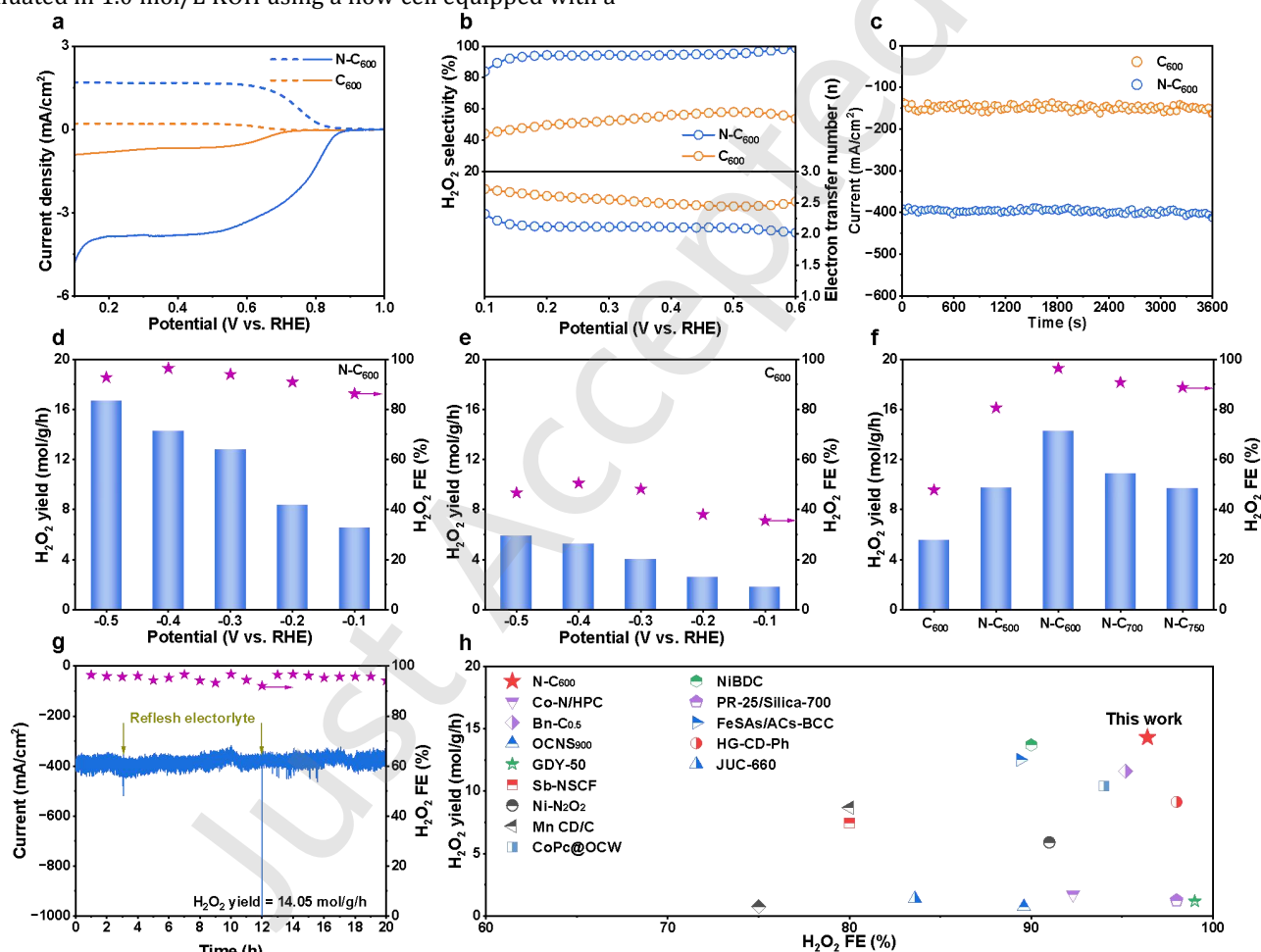


Fig. 3. Electrocatalytic performance. (a) RRDE measurements for ORR at O_2 atmosphere in 1.0 mol/L KOH solution (dash line: disk current and solid line: ring current), (b) corresponding H_2O_2 selectivity and electron transfer number of C_{600} and $N-C_{600}$ samples. (c) Current density of $N-C_{600}$ and C_{600} samples at -0.4 V . H_2O_2 yield and FE of (d) $N-C_{600}$ and (e) C_{600} samples at different potentials. (f) H_2O_2 yield and FE of samples (different graphitic N: pyridinic N) at -0.4 V . (g) Continuous long-term stability tests of $N-C_{600}$ sample at -0.4 V . (h) Comparison of H_2O_2 FE and yield on $N-C_{600}$ sample with those reported in the literature [14,15,35-45]. Typical reaction conditions: 0.5 mg catalyst, 50 mL 1.0 mol/L KOH solution, 40 mL/min O_2 , 1.0 h , 25°C .

As shown in Fig. S16 in the ESM, both H_2O_2 yield and FE increase gradually with increasing N-doping content and reach their maximum values for the N_4-C_{600} sample, further demonstrating the significant effect of N-doping on ORR performance. The influence of O_2 flow rate, KOH concentration, and catalyst loading on the electrocatalytic ORR performance of $N-C_{600}$ was investigated. As shown in Fig. S17 in the ESM, the H_2O_2 yield increases gradually with

increasing O_2 flow rate, while the FE first increases and then decreases slightly. As shown in Fig. S18 in the ESM, the H_2O_2 yield increases significantly as the KOH concentration increases from 0.1 to 1.0 mol/L , whereas the FE remains above 75% across most concentrations. Both H_2O_2 yield and FE exhibit a volcano-shaped trend with increasing KOH concentration, reaching their maxima in 1.0 mol/L KOH solution. Similar volcano-shaped trends for both H_2O_2 yield

and FE are observed with increasing catalyst loading, with maxima at 0.5 mg/cm² (Fig. S19 in the ESM). The electrocatalytic ORR reaction on bare carbon paper (without any catalyst) at -0.4 V vs. RHE was also conducted to investigate the origin of H₂O₂. As expected, only trace H₂O₂ was detected after the reaction, confirming that the contribution from bare carbon paper is minimal and that the active material is the N-C₆₀₀ catalyst. A control sample (prepared by pyrolysis of PVP alone) was also characterized, and its ORR performance was evaluated (Figs. S20-S22 in the ESM). The H₂O₂ yield and FE of this control sample are 5.33 mol/g/h and 67.8%, respectively, which are much higher than those of C₆₀₀ sample, indicating the synergistic effect of graphitic N and pyridinic N on 2e⁻ ORR performance. Similar but slightly lower results are obtained for both C₆₀₀ and N-C₆₀₀ samples under air atmosphere at various potentials (Fig. S23 in the ESM). To investigate the role of graphitic N and pyridinic N in ORR performance, electrocatalytic ORR experiments were conducted on various N-C samples. As the graphitic N content increases, both H₂O₂ yield and FE first increase and then slightly decrease, reaching their maximum values for the N-C₆₀₀ sample (Fig. 3(f)). The slightly decrease of both H₂O₂ yield and FE is owing to the excessive graphite N and less pyridine N content, indicating the significant synergistic effect of graphitic N and pyridinic N on 2e⁻ ORR performance. Finally, continuous long-term stability tests at high current density

of N-C₆₀₀ sample were conducted, as shown in Figs. 3(g). The current density and H₂O₂ FE remain stable over 20 h, accoupling with high H₂O₂ yield. After long-term stability tests, the catalytic activity, H₂O₂ selectivity and surface nitrogen configurations were examined and shown in Fig. S24 in the ESM, indicating that the structure with a graphitic N to pyridinic N ratio of 2:4 in graphitic carbon offers excellent stability. Remarkably, N-C₆₀₀ demonstrates one of the highest reported performances for the electrocatalytic ORR to date, achieving outstanding H₂O₂ yield, FE, and current density (Fig. 3(h) and Table S2 in the ESM) [14,15,35-45].

2.3 Reaction mechanism

To evaluate the O₂ adsorption site, oxygen temperature-desorption (O₂-TPD) measurement is conducted. As shown in Fig. S25 in the ESM, only one adsorption peak at around 250°C is detected for the C₆₀₀ sample, corresponding to O₂ adsorption at carbon sites. After N-doping, a single adsorption peak appears at approximately 318-331°C for all N-C samples, while the peak at 250°C disappears. Notably, the adsorption peak shifts to a higher temperature with increasing graphitic N content (*i.e.*, with increasing pyrolysis temperature). This indicates that the presence of graphitic N significantly promotes O₂ adsorption on the neighboring carbon site.

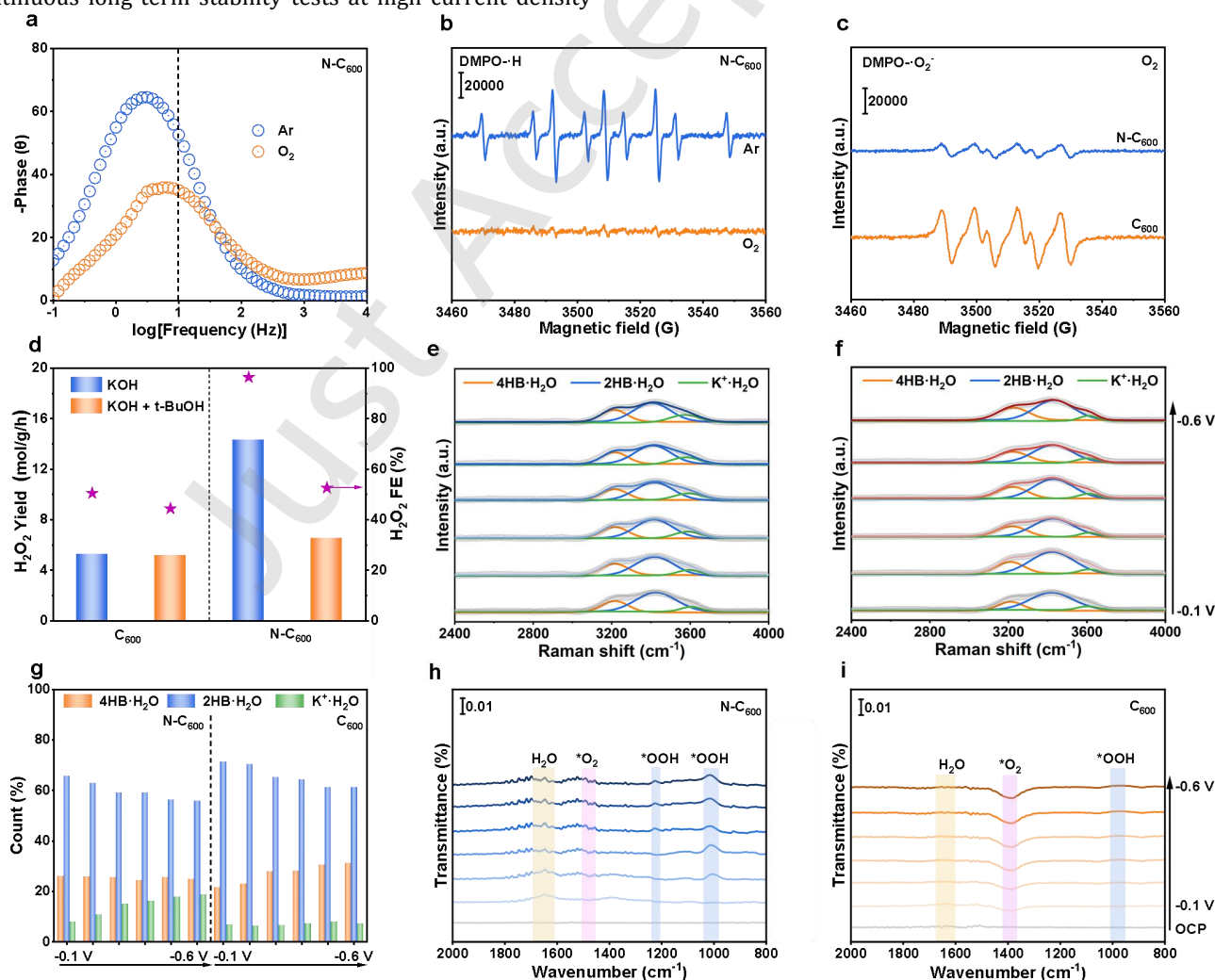


Fig. 4. Reaction mechanism. (a) Bode plots of N-C₆₀₀ at -0.4 V under Ar/O₂ atmosphere. (b) In situ EPR spectra of N-C₆₀₀ at -0.4 V under Ar/O₂

atmosphere. (c) In situ EPR spectra of C_{600} and N- C_{600} samples at -0.4 V with addition of CH_3OH under O_2 atmosphere. (d) H_2O_2 yield and FE comparison of N- C_{600} at -0.4 V in KOH with or without addition of t-BuOH to capture $\bullet H$. In situ Raman spectra of the O-H stretching mode of interfacial H_2O on (e) N- C_{600} and (f) C_{600} samples at various potentials (-0.1 to -0.6 V). (g) Potential-dependent count of interfacial H_2O on N- C_{600} and C_{600} samples at various potentials (-0.1 to -0.6 V). In situ FT-IR spectra on (h) N- C_{600} and (i) C_{600} samples at various potentials (-0.1 to -0.6 V).

The generation of $\bullet H$ species during the reaction is probed by EIS combined with Bode phase analysis. During the ORR, the competing hydrogen evolution reaction (HER) proceeds *via* three elementary steps: the Volmer step ($H_2O + e^- \rightarrow \bullet H + OH^-$), the Heyrovsky step ($\bullet H + H_2O + e^- \rightarrow H_2 + OH^-$), and the Tafel step ($\bullet H + \bullet H \rightarrow H_2$) [46,47]. In the Bode phase plots, the peak position reflects the dominant kinetic process, while the peak intensity correlates with the interfacial charge transfer rate [48]. Typically, low-frequency (10^{-1} - 10^1 Hz) and mid-frequency (10^1 - 10^2 Hz) regions are associated with the Volmer and Heyrovsky steps, respectively, whereas the Tafel step is not electrochemically distinguishable due to the absence of electron transfer. As shown in **Fig. S26** in the ESM, the phase angle peaks of all N-C samples are located in the low-frequency region, in contrast to the C_{600} sample, which exhibits a peak in the mid-frequency range. This shift indicates that nitrogen doping promotes a transition from a Heyrovsky-dominated process to a Volmer-dominated process. Moreover, the peak intensity decreases progressively with increasing pyridinic N content, suggesting accelerated interfacial kinetics and enhanced $\bullet H$ generation *via* the Volmer step. Furthermore, Bode plots of the N- C_{600} sample at -0.4 V vs. RHE under O_2 and Ar atmospheres (**Fig. 4(a)**) reveal a further shift and attenuation of the phase peak under O_2 , indicating that the generated $\bullet H$ species are continuously consumed by O_2 . Consistently, the Nyquist plots (**Fig. S27** in the ESM) show a reduced charge transfer resistance with increasing pyridinic N content, corroborating the facilitated Volmer step and enhanced $\bullet H$ generation.

To further probe H_2O dissociation experimentally, in situ EPR is conducted using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) to capture generated radicals at -0.4 V vs. RHE under O_2 and Ar atmospheres, respectively. As shown in **Fig. S28** in the ESM, nine distinct peaks with an intensity ratio of 1:1:2:1:2:1:2:1:1 are observed for all the N-C samples under Ar atmosphere, corresponding to the characteristic signals of $\bullet H$, whereas no DMPO- $\bullet H$ signal is observed for the C_{600} sample [49]. The DMPO- $\bullet H$ signal intensity gradually increases with increasing pyridinic N content, suggesting that pyridinic N promotes efficient H_2O dissociation for $\bullet H$ generation. It's shown in previous study that the lone pair electrons of pyridinic nitrogen can promote water dissociation in the Volmer step and provide a stable anchoring site for $\bullet H$ (from p-N to p-N-H) [16]. Notable, the DMPO- $\bullet H$ signal intensity of the N- C_{600} sample significant decreases when the reaction is carried out under O_2 atmosphere (**Fig. 4(b)**), indicating that the generated $\bullet H$ participates in the $2e^-$ ORR and is largely consumed. The DMPO- $\bullet O_2^-$ signal is also detected for both C_{600} and N- C_{600} samples under O_2 atmosphere with addition of CH_3OH . Notably, the DMPO- $\bullet O_2^-$ signal intensity for the N- C_{600} sample is significantly lower than that of the C_{600} sample (**Fig. 4(c)**), indicating suppressed formation of the $\bullet O_2^-$ intermediate on N- C_{600} sample. Considering the excellent performance of N- C_{600} sample on $2e^-$ ORR, O_2 reduction on N-

C_{600} might proceed *via* a direct hydrogenation pathway, in which adsorbed O_2 is converted to $\bullet OOH$ through coupling with $\bullet H$ species in a single step, bypassing the $\bullet O_2^-$ intermediate. In contrast, the stronger $\bullet O_2^-$ signal observed on the C_{600} sample indicates that O_2 reduction proceeds through a superoxide-mediated pathway, in which $\bullet O_2^-$ serves as a key intermediate prior to $\bullet OOH$ formation. This behavior is characteristic of PCET mechanism, highlighting the distinct reaction pathways on the two catalysts.

To further clarify the involvement of proton/hydrogen-transfer process, kinetic isotope effect (KIE) of H_2O/D_2O (H/D) experiments and scavenging experiments were conducted over C_{600} and N- C_{600} samples at -0.4 V. The KIE value defined as the ratio of H_2O_2 FE in H_2O and D_2O reflects whether the H_2O dissociation is the rate-determining step [50]. The higher the KIE value, the more affection of the catalyst by water dissociation. C_{600} sample shows much lower KIE value of 1.07 than that of N- C_{600} sample (1.53), implying the presence of N species could enhance the dissociation of water and supply sufficient $\bullet H$ for O_2 -to- H_2O_2 reaction. Scavenging experiments were conducted by electrocatalytic ORR performance in a flow cell at -0.4 V with the addition of tert-butanol (t-BuOH) to capture $\bullet H$ species. As shown in **Fig. 4(d)**, the H_2O_2 yield and FE of N- C_{600} decrease significantly after t-BuOH addition (from 14.3 mol/g/h and 96.4% to 6.49 mol/g/h and 52.5%), whereas those of the C_{600} sample remain almost unchanged, indicating the outstanding contribution of $\bullet H$ to the $2e^-$ ORR. In summary, these above results collectively demonstrate the hydrogenation pathway transition (from PCET to AHT process) in O_2 -to- H_2O_2 reaction on N- C_{600} sample owing to the $\bullet H$ generation.

The structure of interfacial water plays a critical role in governing the hydrogenation pathway and the H_2O activation [51]. To investigate the mechanism of H_2O_2 generation and probe the structure of interfacial water, in situ Raman spectroscopy is further employed. As shown in **Figs. 4(e)** and **4(f)**, a broad band in the range of 3000-3800 cm^{-1} is assigned to the O-H stretching vibration of H_2O and deconvoluted by Gaussian fitting into three different modes: four-coordinated hydrogen-bonded water (4HB- H_2O , strong adsorption), two-coordinated hydrogen-bonded water (2HB- H_2O , moderate adsorption), and K^+ -hydrated water ($K^+ \cdot H_2O$, weak adsorption), centered at approximately 3200, 3400 and 3600 cm^{-1} , respectively [51,52]. As the applied potential increases from -0.1 to -0.6 V vs. RHE, the N- C_{600} sample exhibits a nearly constant fraction of 4HB- H_2O , a decrease in 2HB- H_2O (65.9% $\rightarrow$ 56.0%), and a pronounced increase in $K^+ \cdot H_2O$ (8.0% $\rightarrow$ 19.0%) (**Fig. 4(g)**). This shift toward weakly hydrogen-bonded water indicates a progressively disrupted hydrogen-bond network, which facilitates H_2O activation and lowers the energy barrier for $\bullet H$ generation, given that $K^+ \cdot H_2O$ is more readily dissociated than strongly hydrogen-bonded water species [53,54]. In contrast, the C_{600} sample shows an increase in 4HB- H_2O (21.6% $\rightarrow$ 31.2%), a decrease in 2HB- H_2O (71.5% $\rightarrow$ 61.3%),

and negligible change in $K^+ \cdot H_2O$, suggesting the formation of a more rigid hydrogen-bond network at the interface [55]. Such a structure hinders H_2O activation and limits $\bullet H$ availability. These observations indicate that nitrogen site engineering modulates the interfacial water structure, promoting a dynamic, weakly hydrogen-bonded environment on N- C_{600} that favors $\bullet H$ generation and supports the AHT pathway. In contrast, the rigid hydrogen-bond network on C_{600} is more consistent with a proton-coupled electron transfer (PCET)-dominated mechanism. To further investigate the mechanism of H_2O_2 generation, in situ FT-IR measurements were conducted on the N- C_{600} and C_{600} samples. As shown in Fig. 4(h), two key peaks appear at 1016 and 1226 cm^{-1} for the N- C_{600} sample, corresponding to the $\bullet OOH$ intermediate [56,57]. With increasing applied potential, the intensity of these $\bullet OOH$ peaks increases, indicating efficient $\bullet OOH$ generation from O_2 via the AHT process. In contrast, the peaks corresponding to the $\bullet OOH$ intermediate on the C_{600} sample are much smaller than those on N- C_{600} (Fig. 4(i)), indicating slow $\bullet OOH$ generation via the PCET process. In summary, the in situ Raman and in situ FT-IR results confirm that N- C_{600} promotes weakly bonded $K^+ \cdot H_2O$ and facilitates $\bullet H$ generation, which in turn enhance the $\bullet OOH$ formation via AHT pathway, whereas the rigid water network on C_{600} favors a PCET-dominated mechanism for O_2 activation.

2.4 DFT calculation

To further support above characterization results, density functional theory (DFT) calculations are performed. The calculated O_2 adsorption energies and model diagrams of O_2 adsorption at possible sites are shown in Figs. S29 and S30 in the ESM, respectively. The calculated O_2 adsorption energy at the carbon site adjacent to graphitic N is -0.069 eV, which is lower than that at other possible adsorption sites. This indicates that O_2 binds more strongly at the carbon sites adjacent to graphitic N. The free energies of the O_2 -to- $\bullet OOH$ process at different sites are also calculated. As shown in Figs. 5(a), S31 and S32 in the ESM, O_2 activation via the $\bullet OOH$ step requires significantly lower energy at the carbon site adjacent to graphitic N (0.59 eV) than at other sites (e.g., graphitic N site, pyridinic N site, carbon site adjacent to pyridinic N, or a pristine carbon site). The free energies of H_2O dissociation via the Volmer step at different sites are also calculated. As shown in Figs. 5(b), S33 and S34 in the ESM, the energy required at the pyridinic N site (-1.22 eV) is significantly lower than that at other sites (e.g., carbon site adjacent to pyridinic N or graphitic N, a pristine carbon site, or a graphitic N site). These results indicate that the carbon site adjacent to graphitic N serves as the site for O_2 adsorption and activation, whereas pyridinic N acts as the site for H_2O dissociation and $\bullet H$ generation.

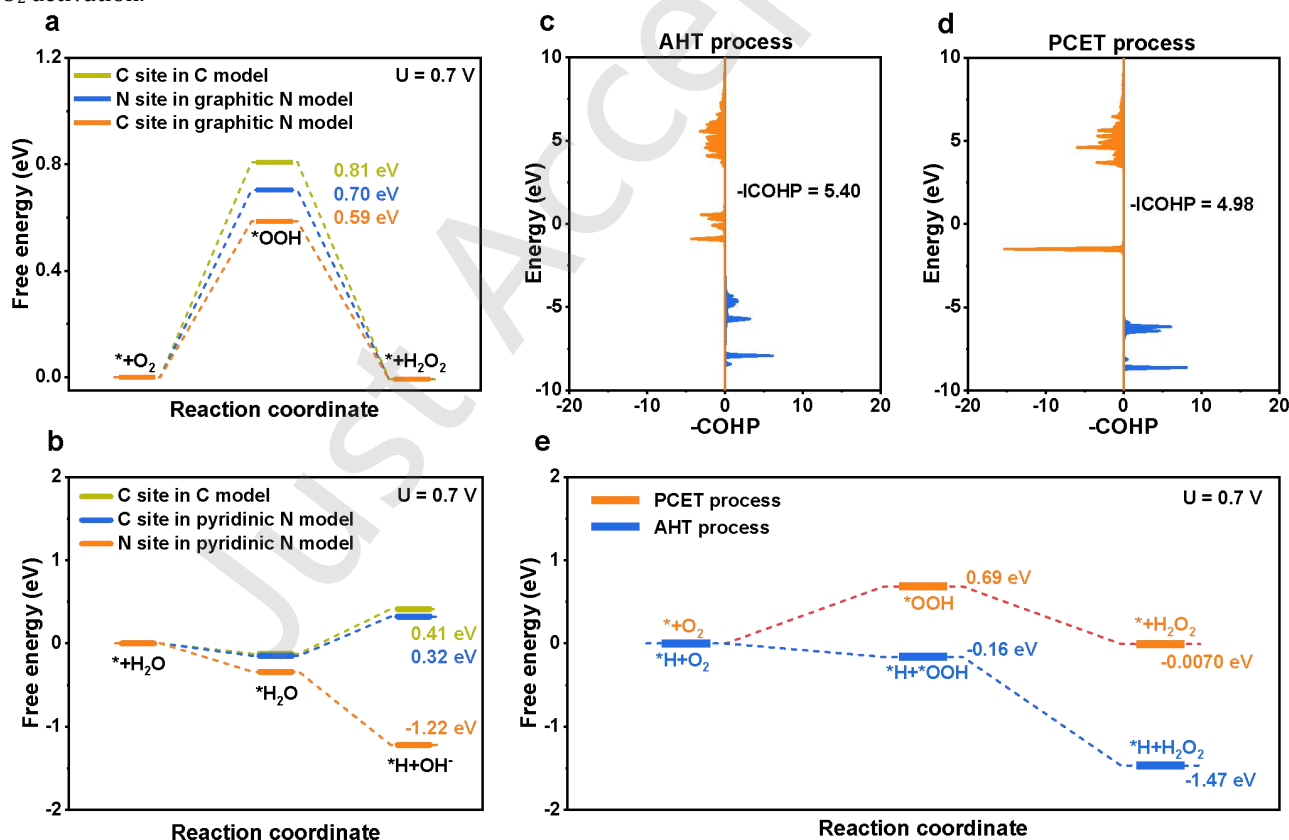


Fig. 5. DFT calculation. Free-energy diagram of (a) O_2 activation pathway at C/N site of C, graphitic N models and (b) H_2O dissociation pathway at C/N site of C, pyridinic N models. The -pCOHP of O-O in adsorbed $\bullet OOH$ intermediates of (c) AHT, (d) PCET process on N- C_{600} model (the blue and orange region represent the bonding and antibonding states, respectively). (e) Free-energy diagram of AHT and PCET process on N- C_{600} sample.

Moreover, the projected crystal orbital Hamilton population (pCOHP) of $\bullet OOH$ adsorbed on the N- C_{600} model is calculated to evaluate the O-O bond strength under the two hydrogenation pathways. As shown in Figs. 5(c) and 5(d), the pCOHP value of the O-O bond under the AHT

pathway is higher than that under the PCET pathway, indicating that the O-O bond is more difficult to break via the AHT pathway in the presence of $\bullet H$, thus avoiding deep hydrogenation to form the byproduct H_2O . Finally, the Gibbs free-energy diagrams for intermediate hydrogenation

through the AHT and PCET processes are constructed for the $2e^-$ ORR. As shown in **Fig. 5(e)**, much higher free energies of 0.69 and -0.0070 eV are required to form $^*OOH$ and $^*H_2O_2$, respectively, on the N-C₆₀₀ model *via* the PCET-mediated pathway. However, with the assistance of $^*H$, the free energies to form $^*OOH$ and H_2O_2 are much lower (-0.16 and -1.47 eV), indicating that hydrogenation occurs more readily *via* the AHT route. The Gibbs free-energy diagram for intermediate hydrogenation on the C₆₀₀ model *via* the PCET process is also calculated, and the results are similar to those on the N-C₆₀₀ model (**Fig. S35** in the ESM). In summary, the pCOHP and Gibbs free energy analyses consistently demonstrate that the AHT pathway strengthens the O-O bond and lowers hydrogenation barriers compared to the PCET pathway, thereby favoring selective $2e^-$ ORR to H_2O_2 .

3. Conclusion

In summary, we have rationally designed engineering hybrid nitrogen-species-doped carbon electrocatalysts, featuring graphitic and pyridinic N sites, to enable efficient electrocatalytic O_2 reduction into H_2O_2 *via* $^*H$ generation at metal-free sites and hydrogenation pathway regulation. In situ characterization and DFT calculations demonstrate that pyridinic N sites facilitate H_2O dissociation to produce $^*H$, whereas graphitic N sites electronically activate adjacent carbon atoms, facilitating efficient O_2 adsorption and activation. The generated $^*H$ participates in the $2e^-$ ORR, regulating hydrogenation pathways of O_2 -to- $^*OOH$ from PCET to AHT process, thereby lowering the free energy for O_2 activation, stabilizing the O-O bond in the $^*OOH$ intermediate, and making H_2O_2 formation thermodynamically more favorable. The as-developed N-C₆₀₀ electrocatalyst displays remarkable $2e^-$ ORR performance, achieving a high H_2O_2 FE and yield of 96.4% and 14.3 mol/g/h at a high current density of approximately 400 mA/cm² *via* the kinetically favorable AHT process, markedly surpassing those of the C₆₀₀ sample (47.8% and 5.54 mol/g/h at current density of ~150 mA/cm²) *via* the PCET process. This study highlights the construction of metal-free hybrid nitrogen-species-doped carbon electro-catalysts for generating $^*H$ and regulating hydrogenation pathways to facilitate electrocatalytic O_2 -to- H_2O_2 conversion.

Methods and data availability

Further details regarding the methods and data (such as TEM, XPS, EPR, O_2 -TPD, electrochemical characterizations and so on) needed to support the conclusions in the paper are presented in the **Electronic Supplementary Material**, available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909238>.

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Author contribution statement

H. Du: Data curation, project administration, validation, writing manuscript, experimental design. R. Shi: Data curation, project administration, validation, experimental design. Y. Fu: Data curation, validation, experimental design. K. Liu: Data curation, experimental design. Z. Cao: Project administration, validation. Y. Zheng: Data curation, validation. Y. He: Data curation, validation. L. Han: Data curation, validation. Y.-C. Cao: Project administration, funding acquisition. B. Jiang: Data curation, project administration, validation, writing manuscript, experimental design, funding acquisition. Y. Yamauchi: Funding acquisition. Hexing Li: Data curation, project administration, validation, writing manuscript, experimental design, funding acquisition.

All the authors have approved the final manuscript.

Declaration of competing interest

All the contributing authors declare no competing interests in this work.

Use of AI statement

None.

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Electronic Supplementary Material

Nitrogen functionalized metal-free catalysts enabling active hydrogen-mediated pathway toward efficient H₂O₂ electro-synthesis

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Chemicals

Citric acid (CA, $\geq 98\%$) and tertiary butanol (t-BuOH) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Polyvinylpyrrolidone ($[(C_6H_9NO)_n]$, PVP-K30), KOH, $Ce(SO_4)_2$, H_2SO_4 and KCl were directly obtained from Macklin Biochemical Technology Co., Ltd. Anhydrous ethanol was purchased from Shanghai Adamas Co., Ltd. and deionized water made by the laboratory was used in all experiments. All the reagents were of analytical grade, and used without further purification.

Catalyst preparation

In a typical synthesis, 4.0 g PVP-K30 and 4.0 g CA were placed in one crucible for use. In the experiment, a lid was added to the crucible to prevent excessive loss of raw materials during the pyrolysis process. Next, place the crucibles filled with raw materials in a tube furnace together. The powder was pyrolyzed under flowing Ar atmosphere in a tube furnace with the following program: from room temperature to $600^\circ C$ at a ramping rate of $2.0^\circ C/min$, then hold at $600^\circ C$ for 180 min, finally the furnace was naturally cooled down to room temperature. After that, take it out, place it in an agate mortar, grind evenly, and weigh to obtain a catalyst. The catalyst was designated as N-C₆₀₀. The preparation of the other N_x-C₆₀₀ samples ($x = 2, 6$) followed the similar general procedure, except that the mass of PVP (2.0, 6.0) in the first step was changed. The C₆₀₀ catalyst was prepared without addition of PVP, all other conditions being the same as for N-C₆₀₀.

Characterization

Structural characteristics

HR-TEM images were collected on a Talos F200s transmission electron microscope, equipped with a Super-X EDS Detector for EDS elemental mapping. The XPS data was obtained K-Alpha X-ray photoelectron spectrometer system (Thermo Scientific) equipped with an Al K α source. The XRD, Raman and FT-IR data were obtained on a D8 FOCUS X-ray diffractometer (Bruker, Cu K α of $\lambda = 0.154$ nm), inVia Raman spectrometer (Renishaw, 532 nm laser) and IS10 Fourier Transform Infrared Spectrometer (Nicolet), respectively. The O₂-TPD were measured on an Microtrac BELCat II instrument (Japan). The UV-visible absorption measurements were performed on a UV7502 spectrophotometer (Shanghai Xinmao).

In situ FT-IR measurement

The in situ FT-IR spectroscopy of photoreduction were carried out using a Nicolet Is10 spectrometer (Thermo Scientific) equipped with an in-situ reaction chamber. The measurements were performed in a standard three-electrode electrochemical cell. A Kapton-tape-sealed window was incorporated into the cell at the working electrode, enabling FT-IR data collection under applied working potentials. Ag/AgCl and Pt wire were used as the work electrode, reference electrode and counter electrode, respectively. The carbon paper coated with catalyst was used for the working electrode, and the electrolyte (1.0 mol/L KOH) was also contained in the cell. The test potential is -0.1 to -0.7 V vs. RHE using CHI 630 instrument (Shanghai, Chenhua, China). Continuously introduce O₂ during the testing process.

In situ EPR measurement

The catalyst sample was placed in an electrochemical cell containing 20 mL of electrolyte, with 1.0 mol/L KOH as the electrolyte. Prior to the experiment, the electrolyte was thoroughly deoxygenated by bubbling Ar gas, followed by purging with a O₂/Ar gas mixture for 20 min to achieve saturation. Constant-potential electrolysis at -0.4 V vs RHE was then carried out in an H-type cell at -0.4 V vs. RHE for 10 min. After electrolysis 5 min, 100 μ L of electrolyte was collected from the cathodic compartment and mixed with 100 μ L of 100 mmol/L DMPO solution. The resulting mixture was loaded into a capillary tube for EPR measurements to detect DMPO- $\bullet$ H signal. When detecting DMPO- $\bullet$ O₂⁻ signal, 5 mL CH₃OH was firstly adding to the resulting mixture. After thorough mixing, the system was loaded into a capillary tube for EPR measurements to detect DMPO- $\bullet$ O₂⁻ signal.

Electrochemical measurements in RRDE

Electrochemical measurements were performed utilizing a three-electrode setup interfaced with a CHI760E electrochemical workstation at ambient temperature. The setup consisted of a catalyst-loaded rotating ring-disk electrode (RRDE) as the working electrode. It featured a 0.247 cm² glassy carbon disk and a 0.186 cm² platinum ring, with a theoretical collection efficiency (N) of 37%. An Ag/AgCl electrode (saturated KCl) served as the reference electrode while a graphite rod functioned as the counter electrode. To prepare the catalyst ink, 4.0 mg catalyst powder was ultrasonically dispersed in the dispersion solvent containing H₂O (285 μ L), ethanol (665 μ L) and Nafion (50 μ L, 5 wt.%) to obtain a homogeneous catalyst ink. Subsequently, a 5.0 μ L of catalyst ink was applied to the disk electrode, with electrochemical testing performed in 1.0 mol/L KOH at 1600 rpm. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were initially performed at a scan rate of 10 mV/s in a O₂-saturated and an Ar-saturated electrolyte. The ring electrode was held at 1.20 V vs. RHE to ensure complete oxidation of generated H₂O₂. The H₂O₂ selectivity and the electron transfer number (n) were quantified according to the disk (I_d) and ring current (I_r) in RRDE measurements, as follows [1]:

$$H_2O_2\% = \frac{200 \times I_r/N}{(-I_d) + I_r/N}$$

$$n = \frac{4 \times (-I_d)}{(-I_d) + I_r/N}$$

Electrochemical measurements in flow cell

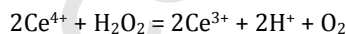
The electrochemical flow cell employed a standard three-electrode system comprising a catalyst-coated gas diffusion electrode (YLS-30T) as the working electrode, a platinum foil counter electrode, and an Ag/AgCl reference electrode (saturated KCl electrolyte). The flow cell employed a Nafion 117 proton exchange membrane to physically separate the cathode and anode compartments while maintaining ionic conductivity. For cathode preparation, a homogeneous catalyst ink was prepared by ultrasonically dispersing 1.5 mg of the catalyst in a mixture containing 20 μ L Nafion solution (5 wt.%) and 230 μ L ethanol/water (7/3 v/v) for 1 h. This well-dispersed ink was then uniformly spray-coated onto the carbon-based gas diffusion electrode with a catalyst loading amount of 0.5 mg/cm². The working electrode featured a geometry area of 1 cm². The flow rate for O₂ gas and 1.0 mol/L KOH electrolyte were 40 and 15 mL/min, respectively. CV and LSV measurements were initially performed at a scan rate of 10 mV/s in a O₂-saturated and an Ar-saturated electrolyte. For durability assessment, the electrolyte was periodically refreshed during extended operation. The flow cell measurements were conducted on an electrochemical workstation (CHI-760, Pine Instruments Co. Ltd, USA) at room temperature. All measured potentials were converted to the reversible hydrogen electrode (RHE) scale based on:

$$E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.0591 \times \text{pH} + 0.197 \text{ V}$$

The electrochemically active surface area (ECSA) was determined by measuring the double-layer capacitance method. CV scans were recorded in a non-faradaic potential range from 0.85 to 0.95 V vs. RHE at multiple scan rates (20, 40, 60, 80, 100 and 120 mV/s). The double-layer capacitance (C_{dl}) was determined from the linear slope of $\Delta j/2$ versus scan rate, where Δj denotes the absolute difference between anodic and cathodic current densities. And this C_{dl} value directly correlates with the ECSA of the electrocatalyst, the slope value was calculated to afford the C_{dl} , which is linearly related to the ECSA.

H₂O₂ yield calculation

The H₂O₂ concentration was determined through redox titration with cerium (IV) sulfate. A titrant solution of 0.50 mmol/L Ce(SO₄)₂ was prepared by dissolving the salt in 0.50 mol/L H₂SO₄ solution. Standard solutions containing Ce⁴⁺ concentrations ranging from 0.04 to 0.40 mmol/L were used to generate a calibration curve by measuring their characteristic absorbance at 320 nm. During the titration process, the distinct color transition from yellow Ce⁴⁺ to colorless Ce³⁺ based on the following equation:



H₂O₂ production was calculated from Ce⁴⁺ reduction data obtained by UV-vis spectroscopy and calibration curve analysis.

The faradaic efficiency (FE) for H₂O₂ generation is calculated as follows [2]:

$$\text{FE}\% = \frac{100 \times \text{mole of generated H}_2\text{O}_2 \times 2 \times 96485}{\text{total consumed charge}}$$

Theoretical calculations

We have employed the first-principles to perform all density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) formulation [3-5]. We have chosen the projected augmented wave (PAW) potentials to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 450 eV [6]. Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method with a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10⁻⁶ eV. A geometry optimization was considered convergent when the energy change was smaller than 0.01 eV Å⁻¹. The vacuum spacing in a direction perpendicular to the plane of the structure is 20 Å for the surfaces. The Brillouin zone integration is performed using 2×2×1 Monkhorst-Pack k-point sampling for a structure. The climbing image-nudge elastic band (CI-NEB) method was used to calculate the diffusion barrier of Li⁺ on the substrates.

The adsorption energies (E_{ads}) were calculated using the equation:

$$E_{\text{ads}} = E_{\text{ad/sub}} - E_{\text{ad}} - E_{\text{sub}}$$

where E_{ad/sub}, E_{ad}, and E_{sub} are the total energies of the optimized adsorbate/substrate system, the adsorbate in the structure, and the clean substrate, respectively.

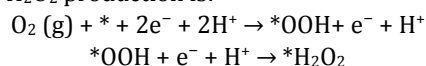
The free energy was calculated using the equation:

$$G = E_{\text{ads}} + \text{ZPE} - \text{TS}$$

where G, E_{ads}, ZPE and TS are the free energy, total energy from DFT calculations, zero-point energy and entropic contributions, respectively.

The entropy correction and the zero-point energy correction at 298.15 K were taken into consideration for the Gibbs free energy. The Gibbs free energy of OOH was calculated based on these of H₂O and H₂ molecules.

The two-electron reaction pathway for H₂O₂ production is:



where * and *OOH denote the catalyst and the intermediate adsorbed on the catalyst, respectively. The free energy changes for the above two-step reactions are calculated based on:

$$\Delta G_{(1)} = \Delta G_{\text{OOH}} - 4.92 \text{ (in eV)}$$

$$\Delta G_{(2)} = 3.56 - \Delta G_{\text{OOH}} \text{ (in eV)}$$

where ΔG_{OOH} represents the adsorption energy of OOH. The activation energy barrier is the maximum of $\Delta G_{(1)}$ and $\Delta G_{(2)}$. The equilibrium potential at standard condition is 0.70 V vs. SHE for two-electron pathway. The crystal orbital Hamilton population calculations were performed to analyze the bonding and antibonding of O-O bond in OOH intermediate.⁶ The charge density difference calculations were performed to unravel the electron transfer.

Just Accepted

Supplementary Figures

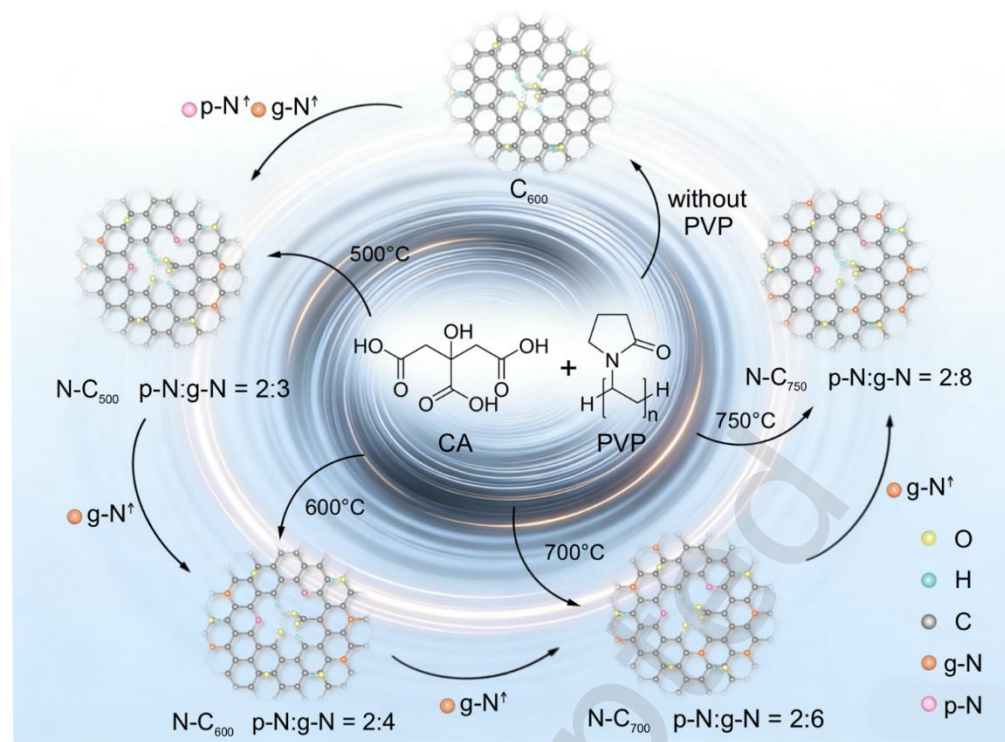


Fig. S1. Schematic diagram and model of the C₆₀₀ and N-C samples preparation pathway (p-N: pyridinic N and g-N: graphitic N).

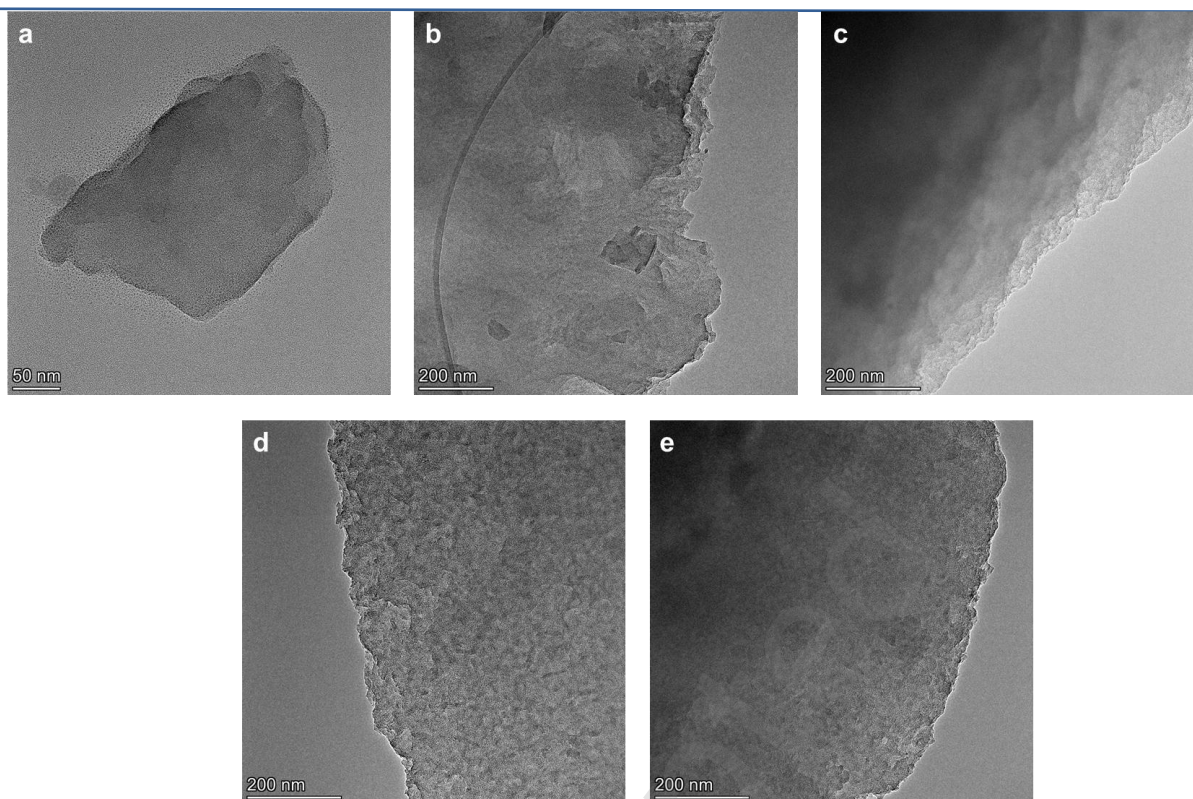


Fig. S2. TEM images of (a) N-C₆₀₀, (b) C₆₀₀, (c) N-C₅₀₀, (d) N-C₇₀₀ and (e) N-C₇₅₀ samples.

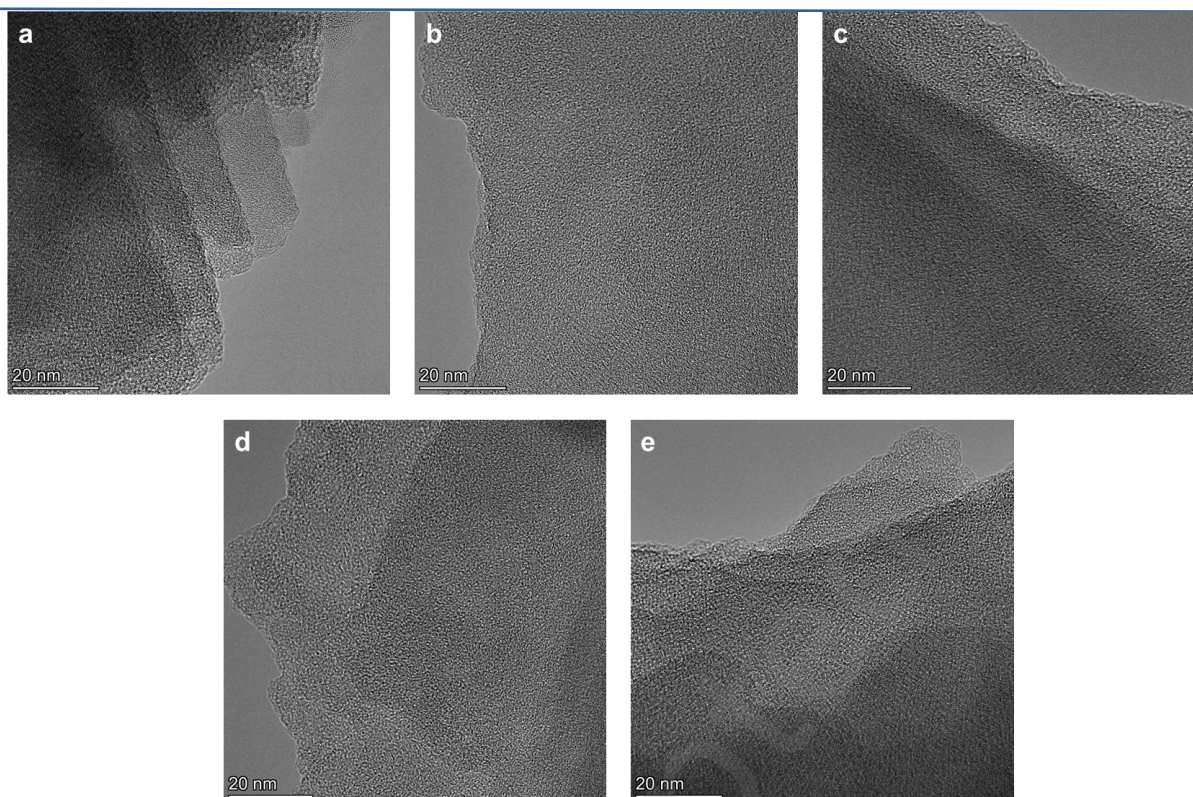


Fig. S3. HRTEM images of (a) N-C₆₀₀, (b) C₆₀₀, (c) N-C₅₀₀, (d) N-C₇₀₀ and (e) N-C₇₅₀ samples.

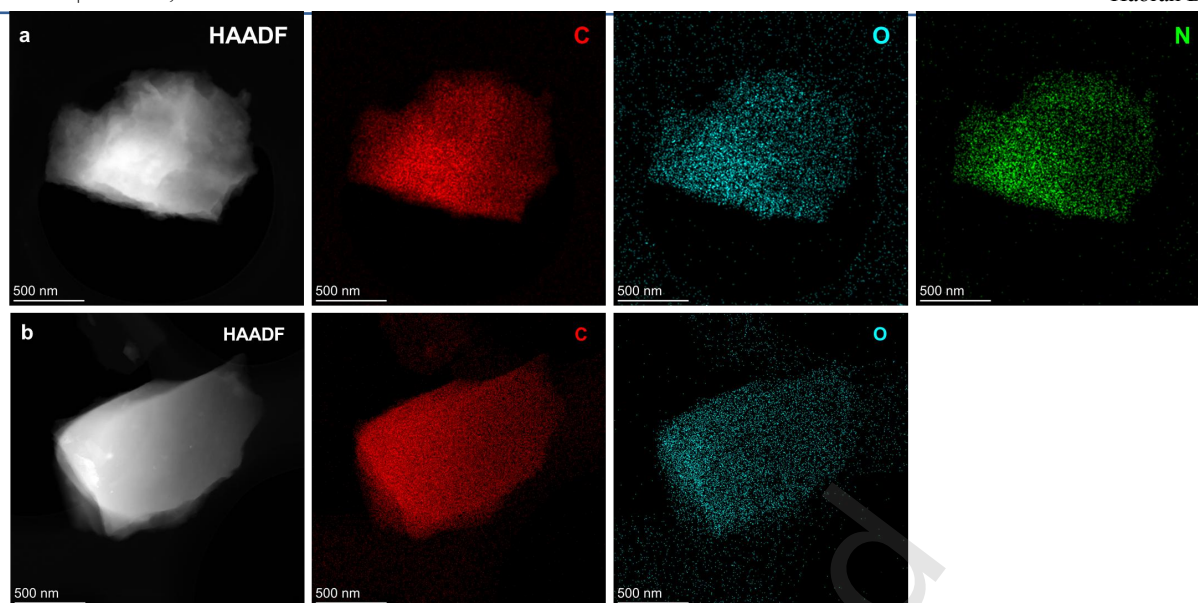


Fig. S4. Element mappings of (a) N-C₆₀₀ and (b) C₆₀₀ samples.

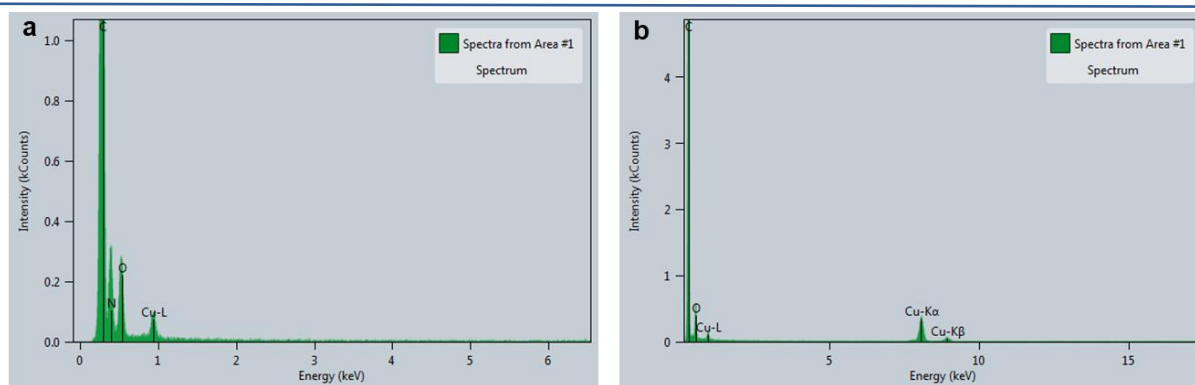


Fig. S5. EDS images of (a) N-C₆₀₀ and (b) C₆₀₀ samples.

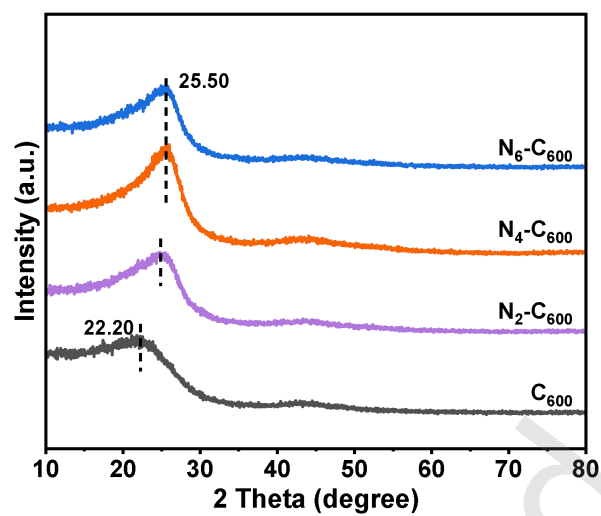


Fig. S6. XRD pattern of C_{600} , N_2-C_{600} , N_4-C_{600} and N_6-C_{600} samples.

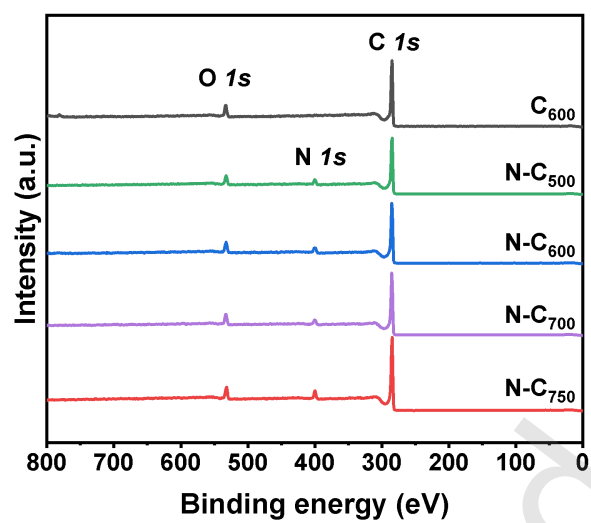


Fig. S7. XPS survey spectra of C₆₀₀, N-C₅₀₀, N-C₆₀₀, N-C₇₀₀ and N-C₇₅₀ samples.

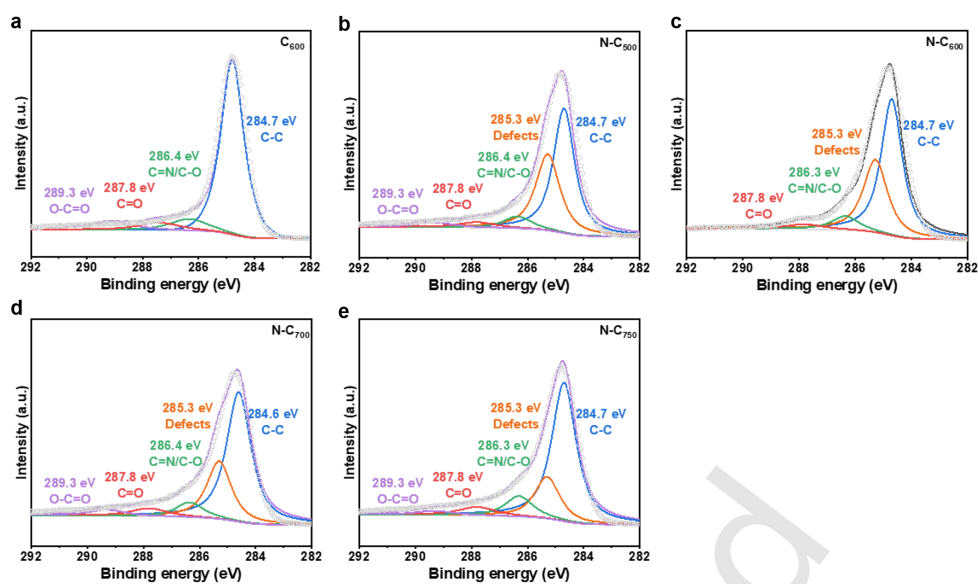


Fig. S8. High-resolution XPS spectra at C 1s level of (a) C₆₀₀, (b) N-C₅₀₀, (c) N-C₆₀₀, (d) N-C₇₀₀ and (e) N-C₇₅₀ samples.

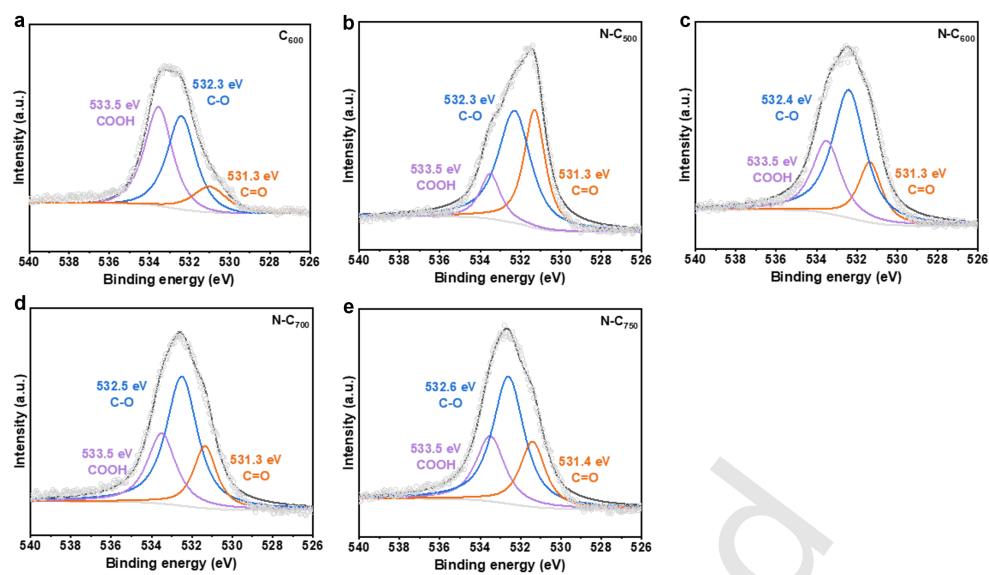


Fig. S9. High-resolution XPS spectra at O 1s level of (a) C₆₀₀, (b) N-C₅₀₀, (c) N-C₆₀₀, (d) N-C₇₀₀ and (e) N-C₇₅₀ samples.

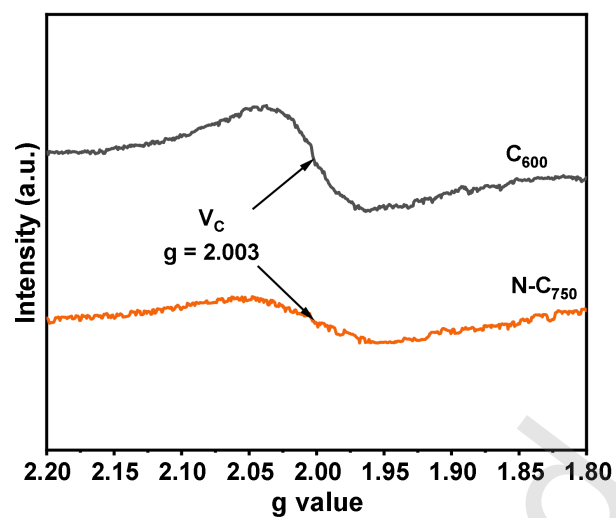


Fig. S10. Vertically expanded EPR spectra of C_{600} and $N-C_{750}$.

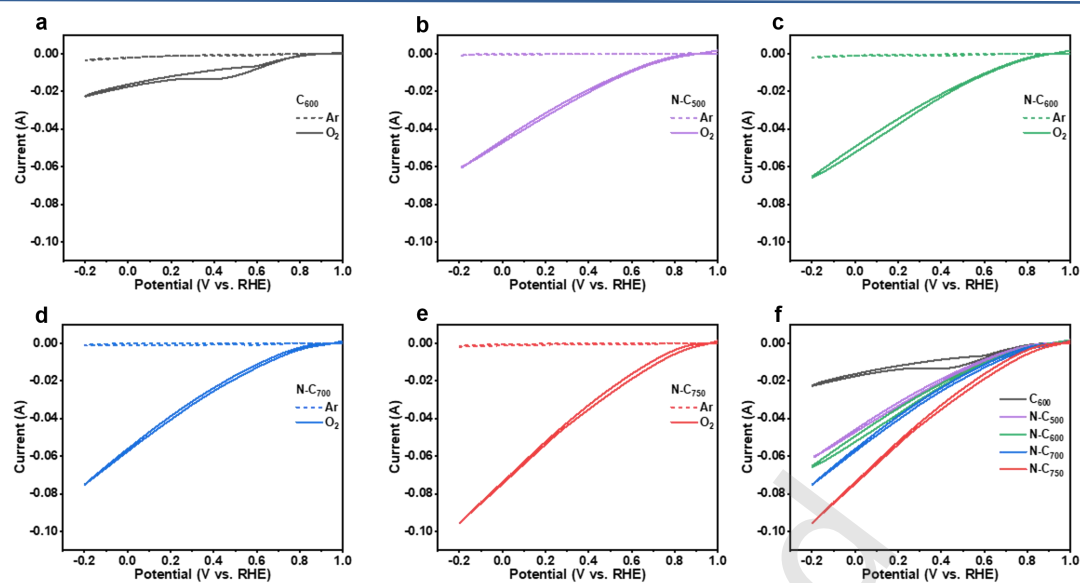


Fig. S11. CV curves of (a) C_{600} , (b) $N-C_{500}$, (c) $N-C_{600}$, (d) $N-C_{700}$ and (e) $N-C_{750}$ samples at O_2 and Ar atmosphere. (f) CV curves comparison of C_{600} and all N-C samples at O_2 atmosphere.

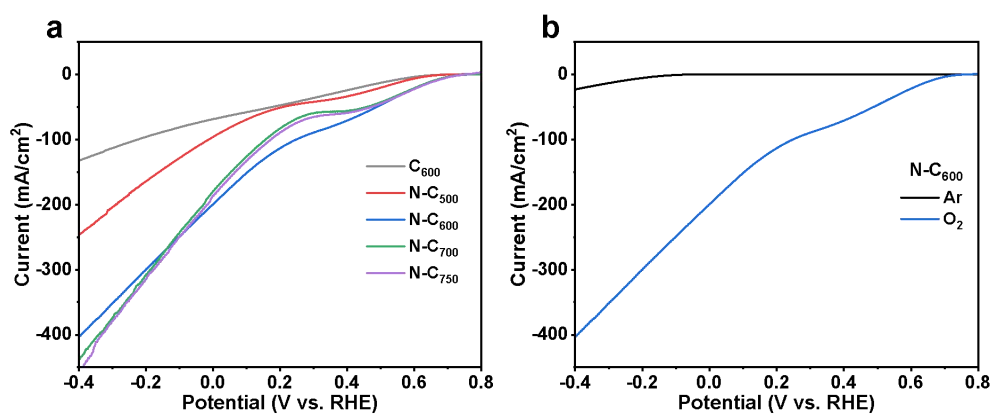


Fig. S12. LSV curves (a) under O₂ atmosphere of C₆₀₀, N-C₅₀₀, N-C₆₀₀, N-C₇₀₀ and N-C₇₅₀ samples and (b) Ar/O₂ atmosphere of N-C₆₀₀ sample.

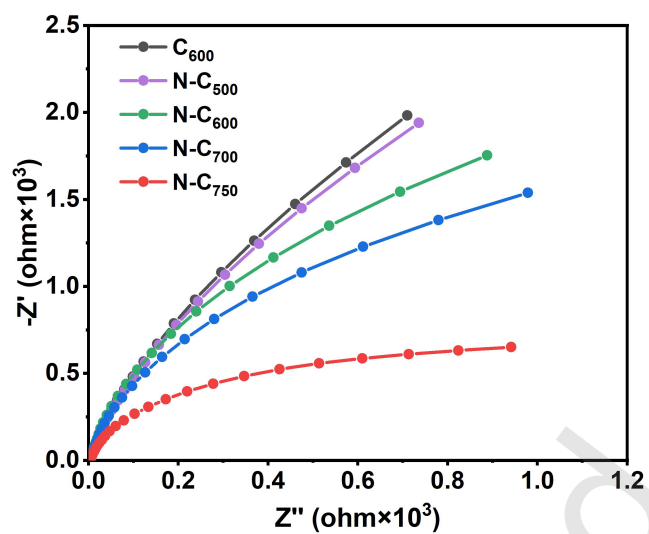


Fig. S13. EIS of C₆₀₀, N-C₅₀₀, N-C₆₀₀, N-C₇₀₀ and N-C₇₅₀ samples under Ar atmosphere.

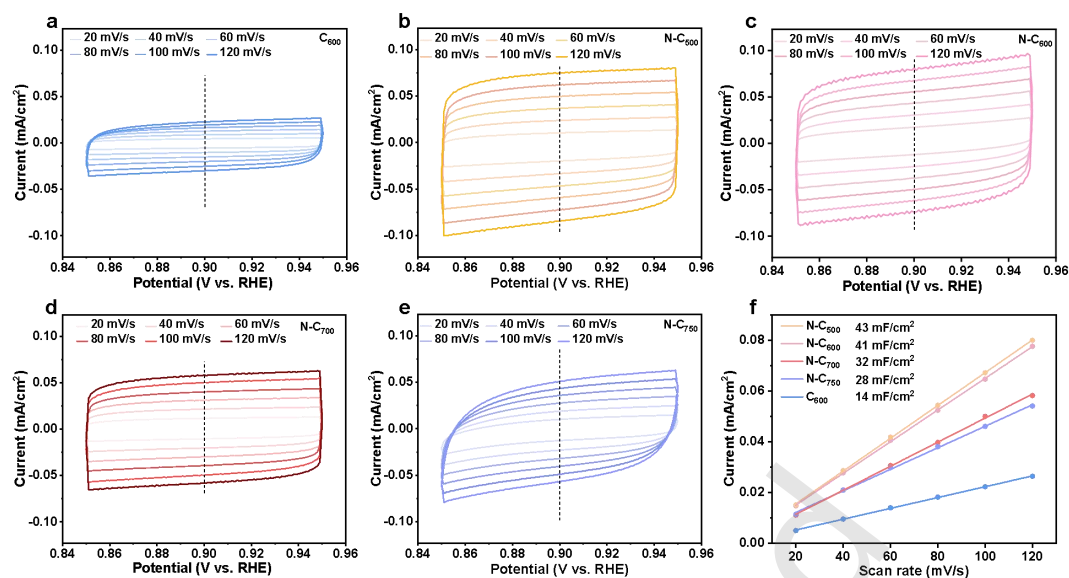


Fig. S14. CV curves of (a) C₆₀₀, (b) N-C₅₀₀, (c) N-C₆₀₀, (d) N-C₇₀₀ and (e) N-C₇₅₀ samples at different scan rate. (f) ECSA analysis of C₆₀₀, N-C₅₀₀, N-C₆₀₀, N-C₇₀₀ and N-C₇₅₀ samples.

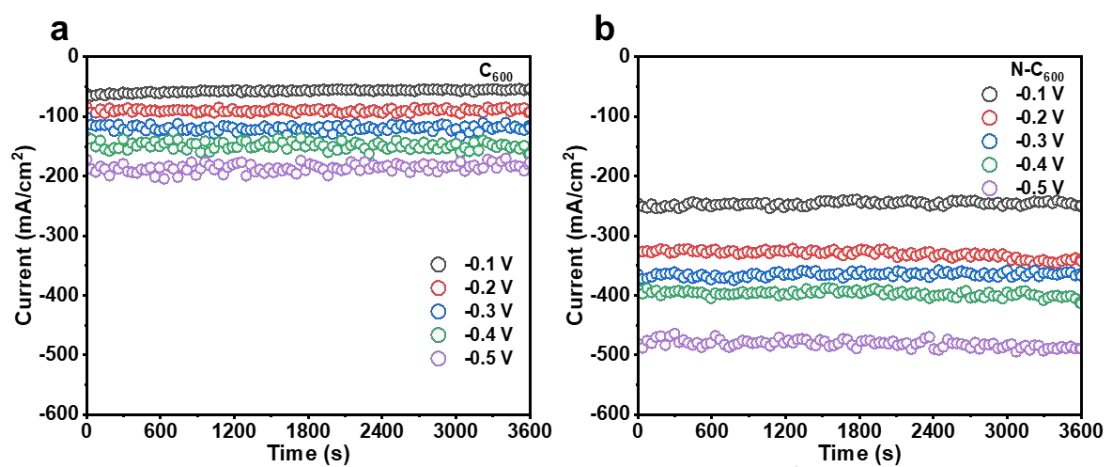


Fig. S15. Current density of (a) C₆₀₀ and (b) N-C₆₀₀ samples at different potentials.

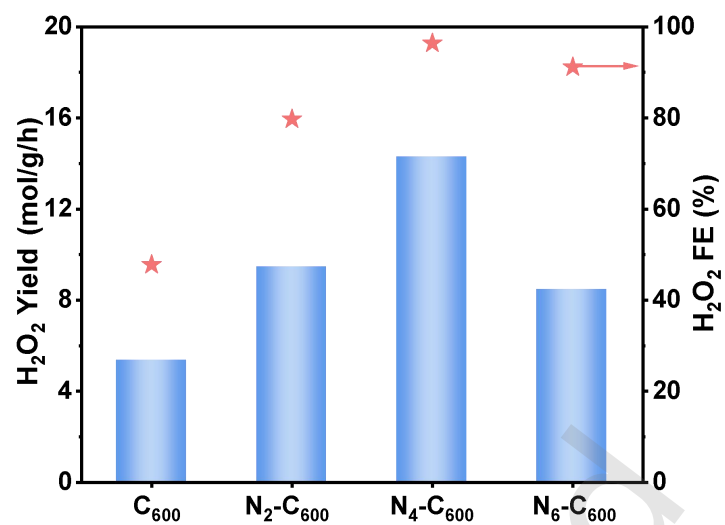


Fig. S16. H₂O₂ yield and FE of different samples at -0.4 V vs. RHE.

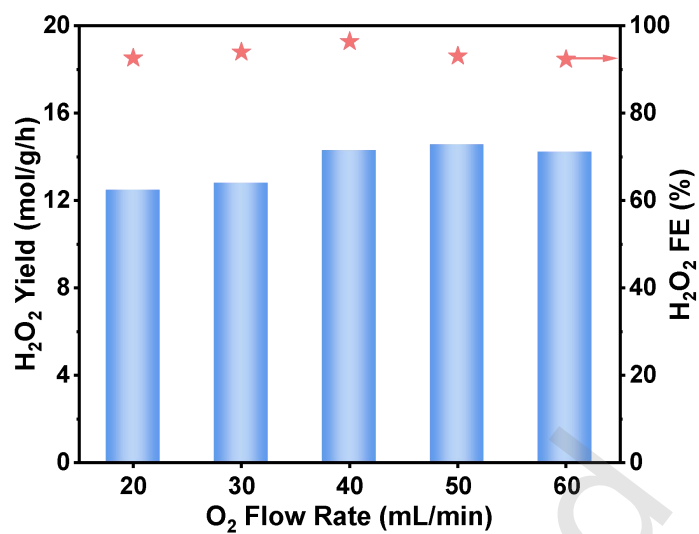


Fig. S17. H₂O₂ yield and FE of N-C₆₀₀ sample with different O₂ flow rate.

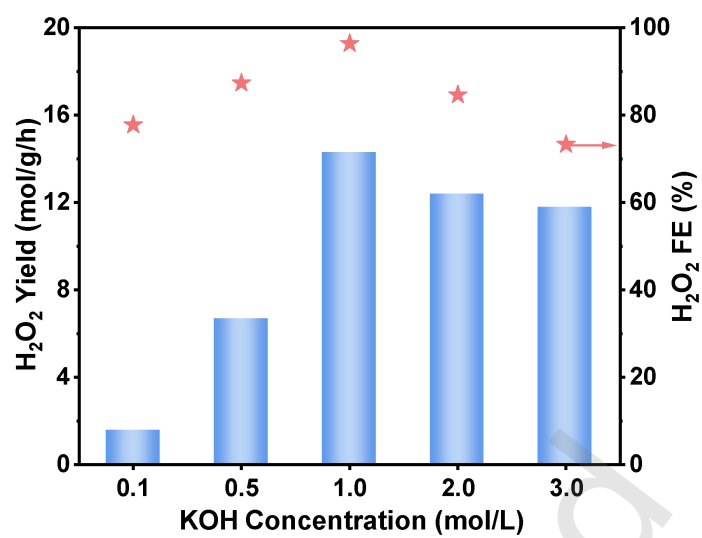


Fig. S18. H₂O₂ yield and FE of N-C₆₀₀ sample in different concentration of KOH solution.

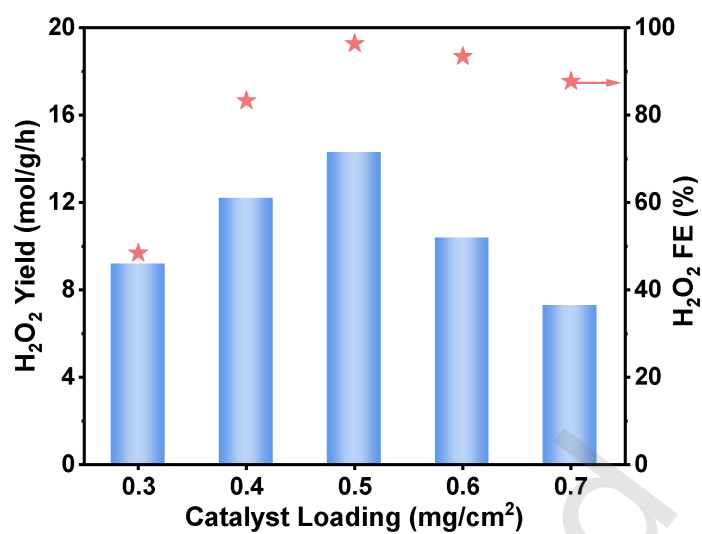


Fig. S19. H₂O₂ yield and FE of different N-C₆₀₀ sample loading.

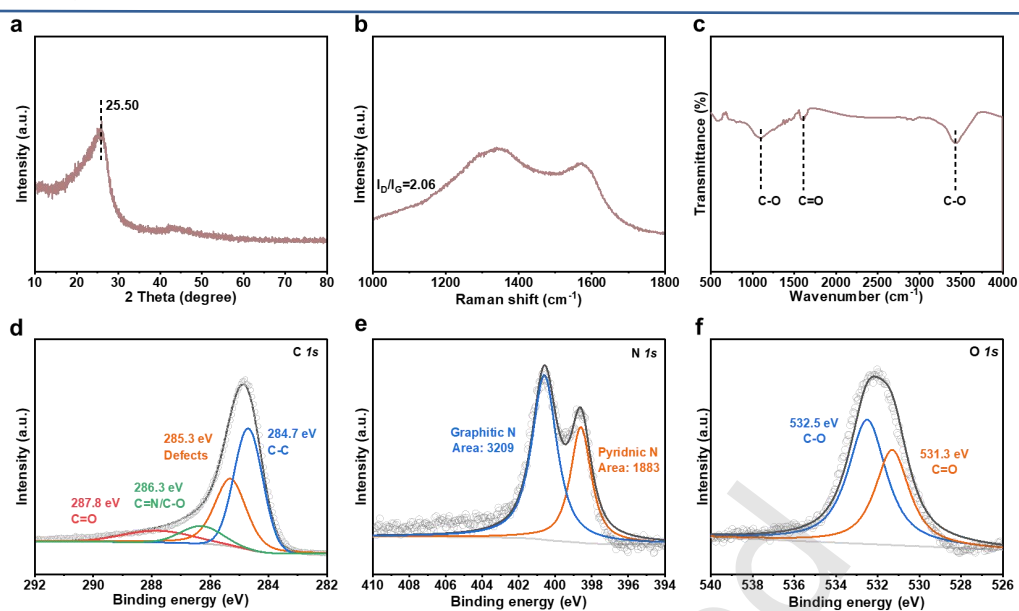


Fig. S20. (a) XRD pattern, (b) Raman spectra, (c) FT-IR and XPS spectra at (d) C 1s, (e) N 1s, (f) O 1s level of control sample (prepared by only PVP pyrolysis).

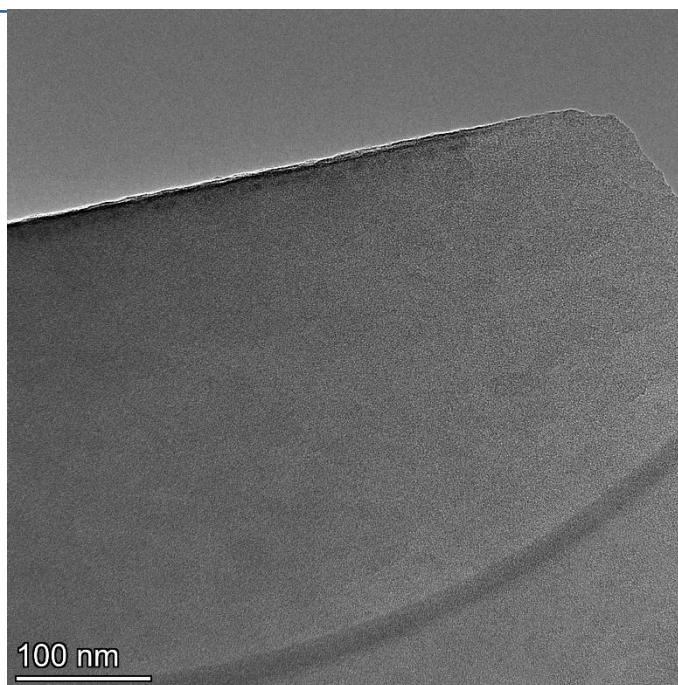


Fig. S21. TEM image of control sample (prepared by only PVP pyrolysis).

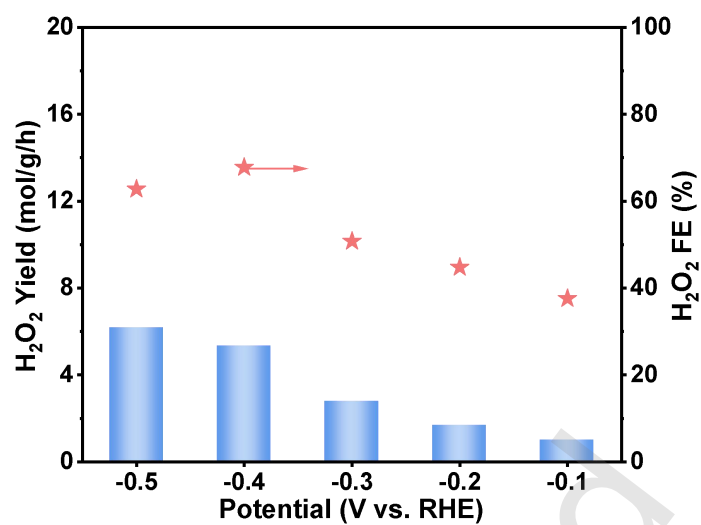


Fig. S22. H₂O₂ yield and FE in O₂ atmosphere at various potentials of control sample (prepared by only PVP pyrolysis).

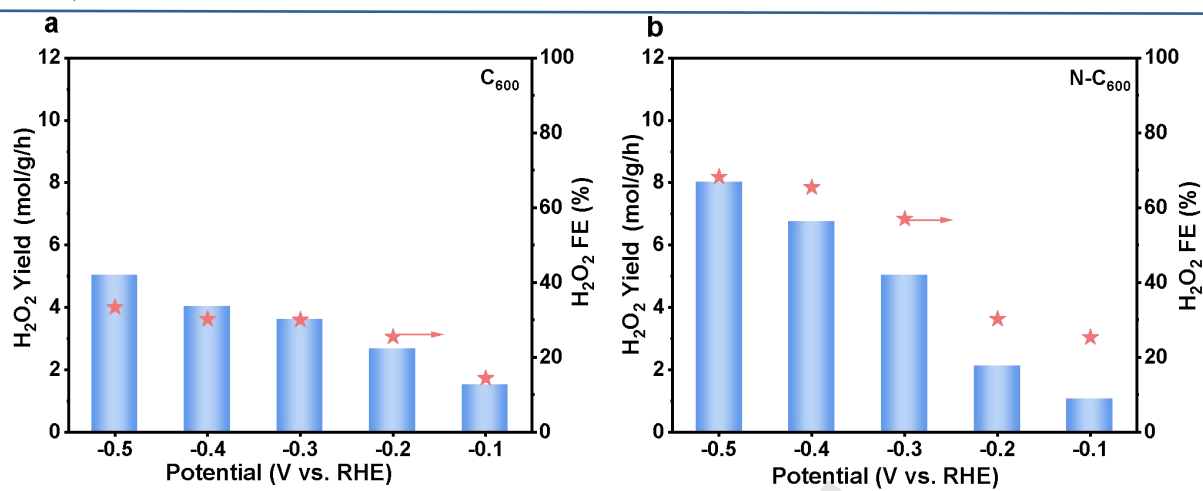


Fig. S23. H_2O_2 yield and FE of (a) C_{600} and (b) N-C_{600} sample under air atmosphere at various potentials.

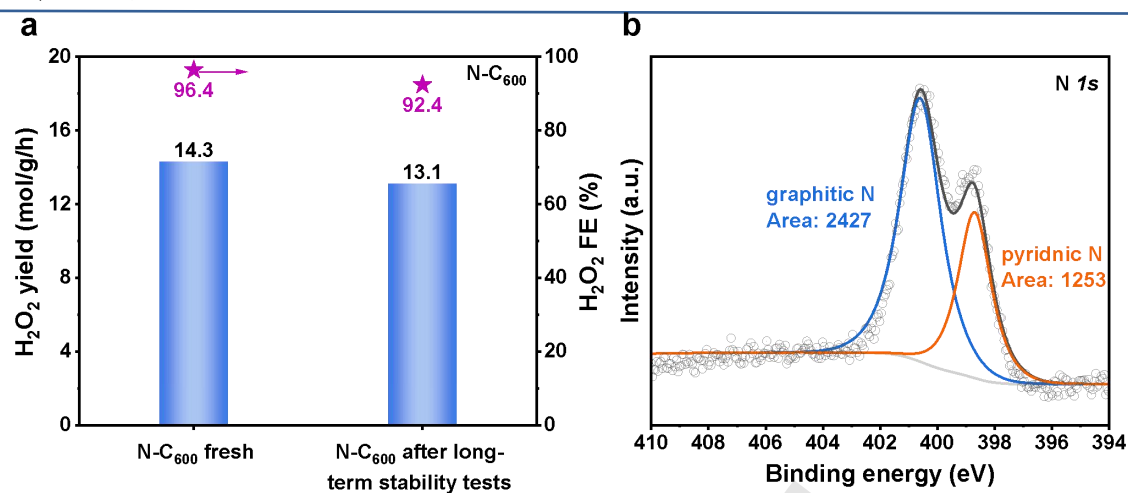


Fig. S24. (a) H_2O_2 yield, FE and (b) XPS at N 1s level of N-C_{600} after 20 h long-term stability tests.

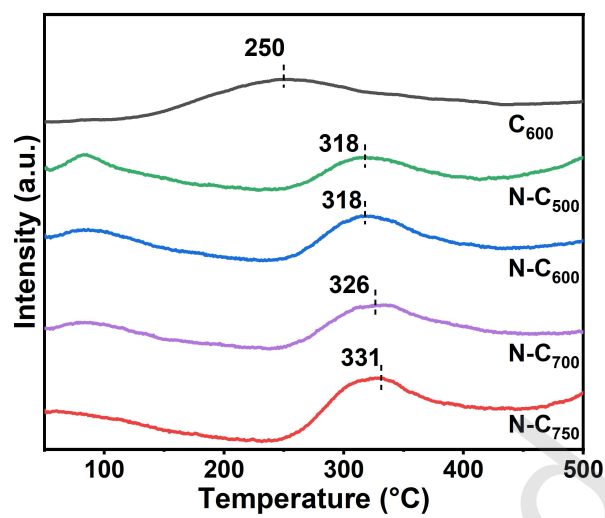


Fig. S25. O₂-TPD of different samples.

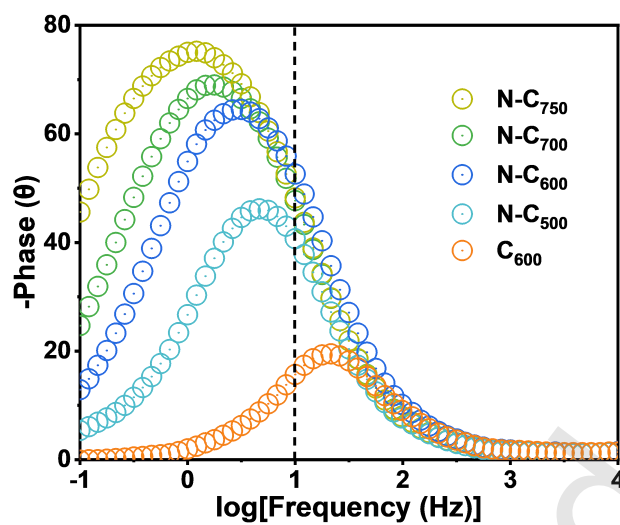


Fig. S26. Bode plots of C₆₀₀, N-C₅₀₀, N-C₆₀₀, N-C₇₀₀ and N-C₇₅₀ samples at -0.4 V vs. RHE under Ar atmosphere.

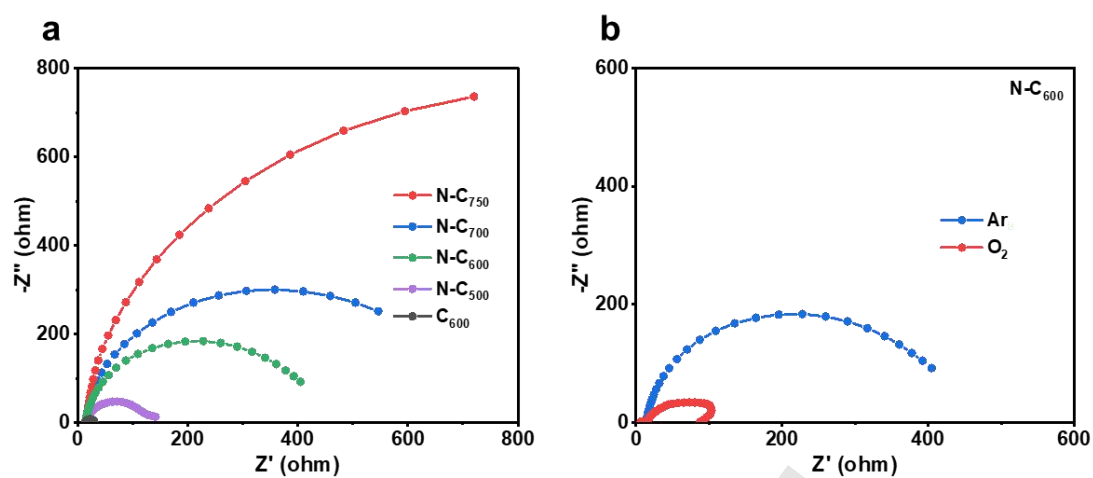


Fig. S27. (a) Corresponding Nyquist plots of C_{600} and all N-C samples in 1.0 mol/L KOH solution at -0.4 V vs. RHE under Ar atmosphere. (b) Nyquist plots of N-C₆₀₀ sample in 1.0 mol/L KOH solution at -0.4 V vs. RHE under Ar/O₂ atmosphere.

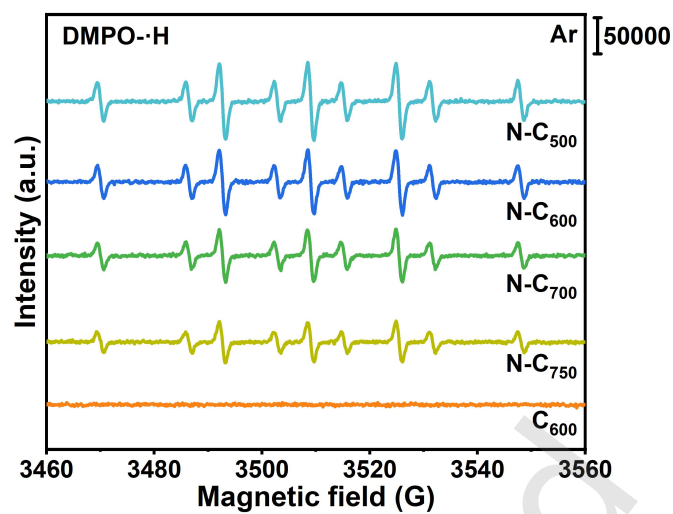


Fig. S28. In situ EPR spectra of different samples under Ar atmosphere at -0.4 V vs. RHE.

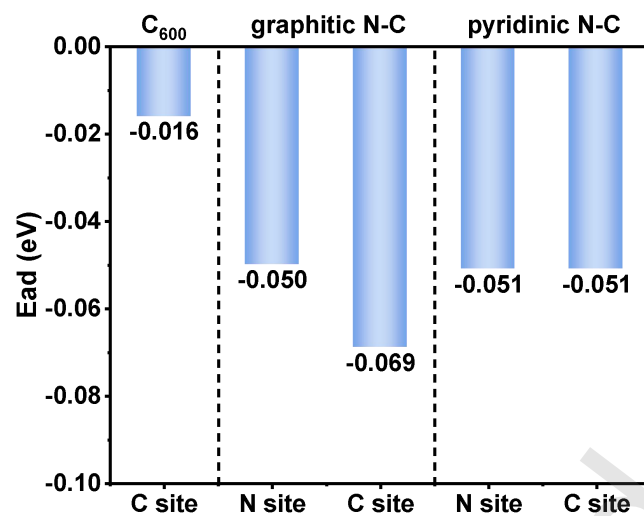


Fig. S29. O_2 adsorption energy diagram at different sites.

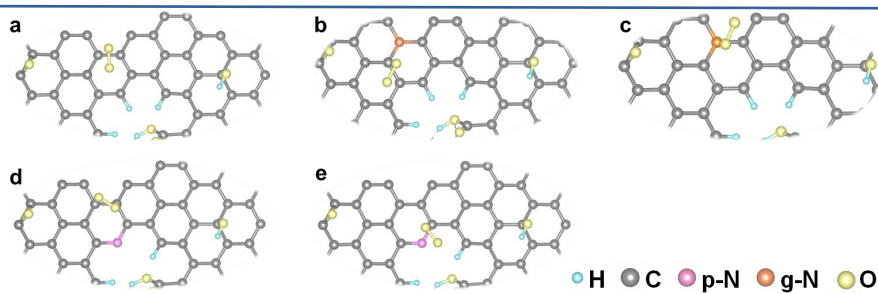


Fig. S30. Model diagrams of O₂ adsorption at (a) C site in C₆₀₀ model, (b) C site and (c) N site in graphitic N-C model, (d) C site and (e) N site in pyridinic N-C model.

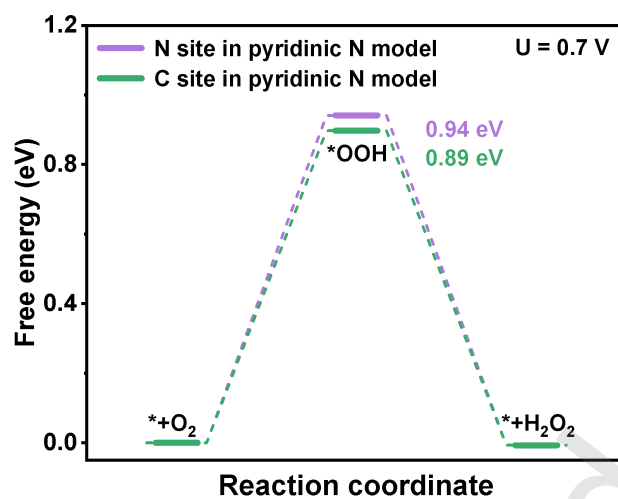


Fig. S31. Free-energy diagram of O_2 activation pathway at C/N site in pyridinic N model.

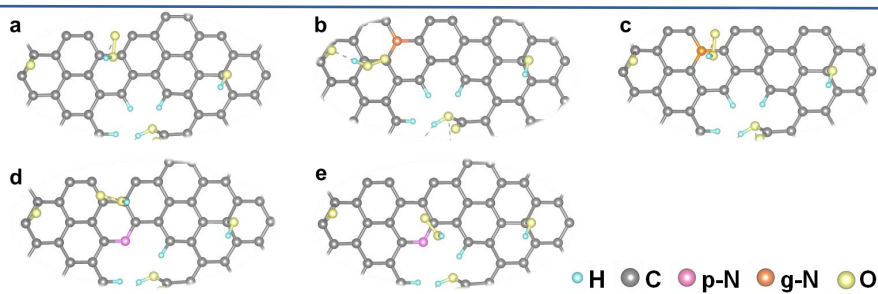


Fig. S32. Model diagrams of *OOH generation at (a) C site in C_{600} model, (b) C site and (c) N site in graphitic N model, (d) C site and (e) N site in pyridinic N model.

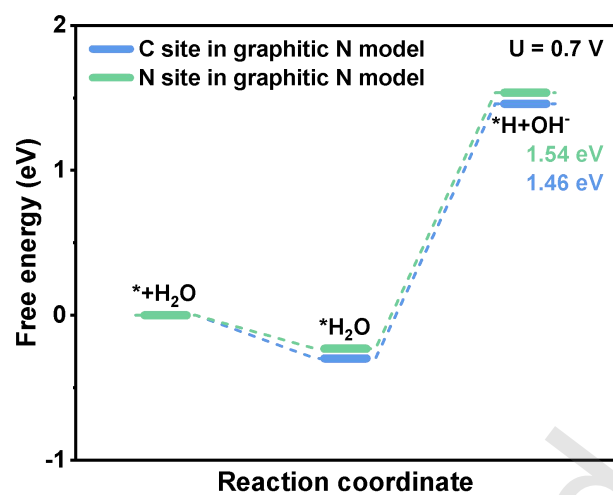


Fig. S33. Free-energy diagram of H₂O dissociation pathway at C/N site in graphitic N model.

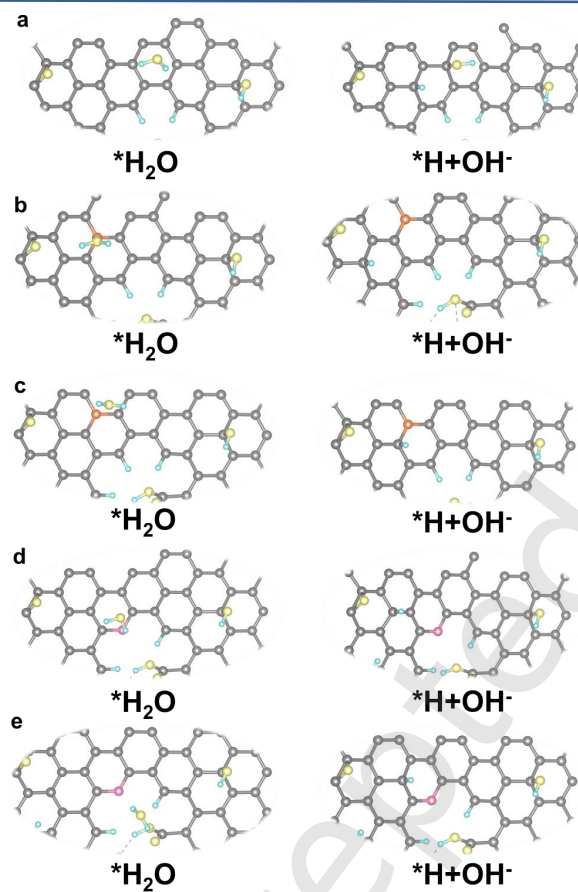


Fig. S34. Model diagrams of H_2O dissociation pathway at (a) C site in C model, (b) C site and (c) N site in graphitic N model, (d) C site and (e) N site in pyridinic N model.

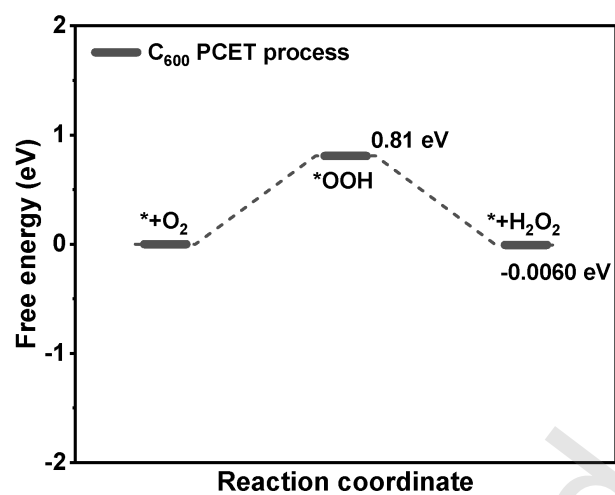


Fig. S35. Free-energy diagram of PCET process on C₆₀₀ sample.

Supplementary TablesTable S1. The C, N, O contents of N-C₇₅₀, N-C₇₀₀, N-C₆₀₀, N-C₅₀₀ and C₆₀₀ samples measured by XPS.

Catalysts	C (atom%)	N (atom%)	O (atom%)
C ₆₀₀	90.7	0.00	9.30
N-C ₅₀₀	86.1	6.09	7.81
N-C ₆₀₀	85.2	7.57	7.23
N-C ₇₀₀	86.0	6.76	7.24
N-C ₇₅₀	85.1	7.01	7.89

Table S2. Comparing the catalytic performance and H₂O₂ production capability between the N-C₆₀₀ and the recently reported electrocatalysts in flow cell.

Catalyst	Electrolyte	Applied Potential (V)	H ₂ O ₂ FE (%)	H ₂ O ₂ Yield (mol/g/h)	Ref.
N-C ₆₀₀	1.0 M KOH	-0.4	96.4	14.3	This work
Sb-NSCF	1.0 M KOH	0.55	80.0	7.46	[12]
Bn-C0.5	1.0 M KOH	0.48	95.2	11.6	[19]
Co-N/HPC	0.1 M KOH	0.80	92.3	1.72	[7]
PR-25/Silica-700	0.1 M PBS	0.0	98.0	1.27	[8]
FeSAs/ACs-BCC	0.1 M KOH	/ ^a	89.4	12.5	[9]
OCNS ₉₀₀	0.1 M KOH	0.75	89.6	0.77	[10]
GDY-50	0.1 M KOH	0.50	99.0	1.20	[11]
Ni-N ₂ O ₂	0.1 M KOH	/ ^b	91.0	5.9	[13]
Mn CD/C	0.1 M KOH	0.786	84.0	8.68	[14]
NiBDC	0.1 M KOH	/ ^c	92.5	13.7	[15]
CoPc@OCW	0.1 M KOH	0.2	94.0	10.4	[16]
HG-CD-Ph	0.1 M KOH	0.4	98.0	9.14	[17]
JUC-660	0.1 M KOH	0.57	83.6	1.40	[18]

^a No applied potential but applied current density of 150 mA/cm² is mentioned.

^b No applied potential but applied current density of 70 mA/cm² is mentioned.

^c No applied potential but applied current density of 200 mA/cm² is mentioned.

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