

Pyridine Functionalized Carbon Nanotubes: Unveiling the Role of External Pyridinic Nitrogen Sites for Oxygen Reduction Reaction

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Pyridinic nitrogen has been recognized as the primary active site in nitrogen-doped carbon electrocatalysts for the oxygen reduction reaction (ORR), which is a critical process in many renewable energy devices. However, the preparation of nitrogen-doped carbon catalysts comprised of exclusively pyridinic nitrogen remains challenging, as well as understanding the precise ORR mechanisms on the catalyst. Herein, a novel process is developed using pyridyne reactive intermediates to functionalize carbon nanotubes (CNTs) exclusively with pyridine rings for ORR electrocatalysis. The relationship between the structure and ORR performance of the prepared materials is studied in combination with density functional theory calculations to probe the ORR mechanism on the catalyst. Pyridinic nitrogen can contribute to a more efficient 4-electron reaction pathway, while high level of pyridyne functionalization result in negative structural effects, such as poor electrical conductivity, reduced surface area, and small pore diameters, that suppressed the ORR performance. This study provides insights into pyridine-doped CNTs-functionalized for the first time via pyridyne intermediates-as applied in the ORR and is expected to serve as valuable inspiration in designing high-performance electrocatalysts for energy applications.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs), which directly generate electricity from hydrogen without CO₂ emission, offer an ultimate solution on achieving the Net Zero targets needed to combat climate change.^[1] One of the major challenges in PEMFCs is the sluggish kinetics of the cathodic oxygen reduction reaction (ORR).^[2] Pt-based electrocatalysts are so far the benchmark catalyst for ORR in commercial PEMFCs.^[3] However, Pt suffers from the high cost, scarce reserve, and poor durability, which limit the implementation of PEMFCs as a long-term solution.^[4] Over the last decade, extensive efforts have been made to develop high-performance and low-cost ORR electrocatalysts.^[5]

Among the many options, metal-free nitrogen-doped carbon materials (NCMs) have shown encouraging ORR performance to replace the Pt-based electrocatalysts.^[6]

Conventional preparation methods of efficient NCMs include chemical vapor deposition^[7] and copolyolysis,^[8] both requiring high-temperature processes above 500 °C. Under such conditions, three types of nitrogen sites (pyridinic, pyrrolic, and graphitic)^[7a] are likely to form simultaneously on the NCMs, resulting in a lack of control over the precise active site(s) for ORR.^[9] Therefore, controllable synthesis of NCMs with selective N sites is required to identify the true active site(s) and to develop efficient ORR electrocatalysts. Guo et al.^[9a] demonstrated that the pyridinic N shows greater ORR activity than graphitic N in acidic electrolyte on the highly oriented pyrolytic graphite (HOPG) model catalysts, which were prepared by treating the HOPG with NH₃ at 700 °C. However, this type of HOPG model catalyst is only valid for conceptual study and is far from commercial utilization. With the purpose of large application of NCMs, further research works are required aimed at developing scalable preparation methods and cheap carbon substrates for advanced pyridinic N-doped electrocatalysts.

Arynes are among the most versatile and well-studied reactive intermediates in organic chemistry.^[10] Typically generated under mild conditions, arynes afford a range of valuable benzenoid and functionalized heterocyclic frameworks that are common motifs in pharmaceuticals, agrochemicals, and organic materials.^[10–11]

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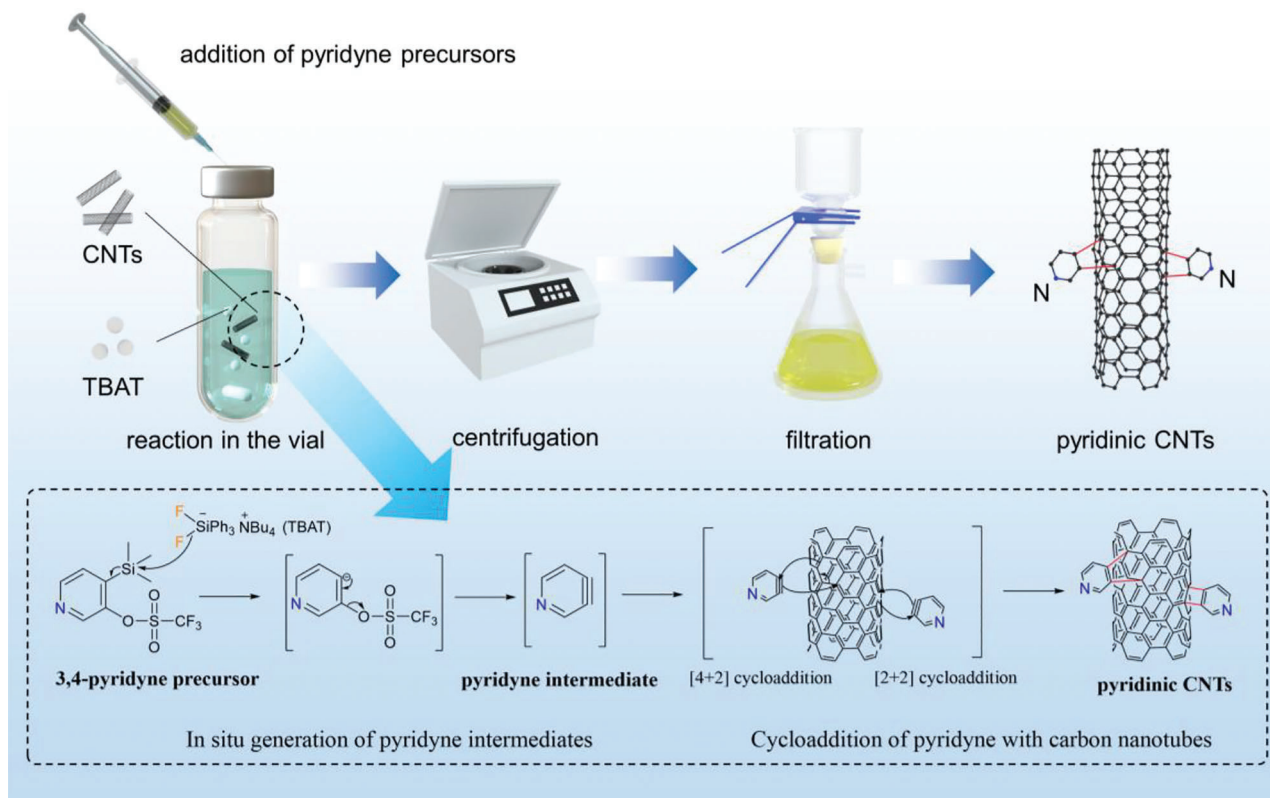
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Scheme 1. Schematic illustration on the preparation of pyridine functionalized CNTs via cycloaddition and corresponding reaction mechanism. The new C— sp^3 bond was highlighted in red.

Benzyne has been shown as a viable reactive intermediate for the functionalization of carbon nanomaterials such as graphene^[12] and carbon nanotubes (CNTs),^[13] enabling the modification of chemical and electronic properties of the graphitic carbon materials. Notably, pyridyne (an *N*-heterocyclic analogue of benzyne) has been used to functionalize graphene and the resulting compounds exhibited comparable ORR catalytic activity to the Pt/C catalyst in alkaline electrolyte.^[14] In comparison to those conventionally prepared N-doped carbon catalysts where the N sites exist in the bulk of the carbon matrix as “internal” nitrogen sites, covalently functionalized pyridinic N sites via cycloaddition provided the “external” pyridinic N sites that are attached outside of the bulk carbon. Benefiting from the mild reaction condition and pre-designed pyridinic N structures, the functionalized N sites are more controllable, which offers more opportunity to design novel catalysts for the conceptual study of pyridinic N sites toward ORR. However, a study of the structure-performance relationships of this type of catalyst, as well as the ORR reaction mechanism itself, has not yet been reported. Furthermore, recent research has revealed that metallic impurities^[15] and intrinsic structural defects^[9b,16] in graphene, such as atom vacancies, dislocations, folds, creases, etc., both lead to great ORR activity in alkaline electrolyte. Therefore, further investigations are required to deconvolute the competing contributions of structural defects, metal impurities, and the *N*-doping to ORR performance, so as to provide more insights into pyridine functionalized carbon materials as ORR catalysts. To this end, high-temperature annealed

CNTs are particularly attractive low-cost substrates to study the intrinsic contribution of pyridinic nitrogen sites, as the metal impurities and defects were eliminated to a lower level. Herein, we report a novel approach to functionalize pyridine with CNTs via pyridyne cycloaddition. A comprehensive investigation was performed to understand the links between the pyridinic N sites, sp^3 C defects, microstructure, reaction mechanisms, and the ORR performance.

In most previous cases where arynes were utilized to functionalize carbon substrates, caesium fluoride (CsF) was used to initiate aryne formation, with an 18-crown-6 ether additive and CH_3CN solvent; in addition, many solvents were used after the reaction to purify the reagents.^[12a,13,14] In this study, CNTs have been functionalized using 4-(Trimethylsilyl)pyridin-3-yl trifluoromethanesulfonate (3,4-pyridyne precursor), with tetrabutylammonium difluorotriphenylsilicate (TBAT) as the only reagent in the reaction for the first time due to its high solubility in organic solution (**Scheme 1**). This innovation also significantly simplifies the purification steps and reduces chemical waste. In addition, the functionalization method via pyridyne cycloaddition allows higher functional degree of the samples compared with related studies (i.e., pyridyne-graphene via and pyridine-CNT via carbene intermediates),^[14,17] thus enabling the investigation of the structures and ORR electrochemistry on samples with different levels of pyridinic N. The results from materials characterization and ORR electrochemistry, combined with density functional theory (DFT) calculations revealed that the ORR

Table 1. Reaction conditions and XPS elemental composition of the prepared samples.

Entry	Sample name	Reaction Conditions			Element composition [at.%]		
		CNTs [mg]	Aryne precursor [mmol]	TBAT [mmol]	C1s	N1s	O1s
1	pristine CNTs	–	–	–	99.44	–	0.56
2	1.13% NCNTs	40 mg	0.1	0.2	97.07	1.13	1.80
3	3.78% NCNTs	40 mg	0.2	0.4	92.55	3.78	3.67
4	8.24% NCNTs	40 mg	0.9	1.8	86.45	8.24	5.31
5	benzene-CNTs	40 mg	0.1 ^{a)}	0.2	98.55	–	1.45
6	blank catalyst	40 mg	0.1	–	98.62	–	1.38

^{a)} (2-(Trimethylsilyl)phenyl trifluoromethanesulfonate was used as benzyne precursor.)

on the pyridinic N functionalized CNTs proceeds via a 2-electron dominated pathway. Intriguingly, functionalization via the pyridyne cycloaddition was found to induce negative structural effects, by changing the electronic properties and the microstructure of the catalysts, which profoundly impacted the ORR behavior.

2. Results and Discussion

Commercially purchased high-purity CNTs (99.9%) used in this work were annealed at high temperature to eliminate the defects in the graphitic layer. In addition, an acceptable value of 33 ppm trace iron was detected by Inductively coupled plasma-optical emission spectroscopy (ICP-OES) in the CNTs. 3,4-pyridyne precursor was used to functionalize the CNTs via cycloaddition as the “external” pyridinic N sites as described in the experimental section (see Supporting Information for the synthesis of 3,4-pyridyne precursor). The level of functionalization was manipulated by tuning the ratio of CNTs and 3,4-pyridyne precursors. This enables a systematic investigation on the structure-performance relationships of the catalysts with different N functional pyridinic degree. In addition, the benzene-CNTs with analogous structure was prepared using benzyne as a precursor to study the ORR catalytic activity without N sites; a blank catalyst was also prepared (i.e., without the addition of TBAT to prevent the formation of the pyridyne intermediate) in order to verify the effect of the thermal cycloaddition on the CNTs properties.

As demonstrated in Scheme 1, 3,4-pyridyne precursor functionalization with the CNTs was achieved in a one-pot reaction involving the in situ generation of 3,4-pyridyne intermediates and subsequent cycloaddition with the CNTs. Initiated by the TBAT, the trimethylsilyl (TMS) group and the trifluoromethanesulfonyl (OTf) group were cleaved to generate a reactive pyridyne intermediate that contains a triple bond within the heteroaromatic ring. Immediately after the generation, the pyridyne intermediates formed new C–C sp^3 bonds (highlighted in red) with the CNTs via either the [2+2] or [4+2] cycloaddition pathway to achieve the pyridine functionalized CNTs.^[18]

2.1. Active Sites and Surface Chemistry

X-ray Photoemission Spectroscopy (XPS) was employed to study the elemental composition and surface chemistry of the prepared

samples. As shown in Table 1, a range of pyridine functionalized CNTs were prepared with N atomic percentage (at.%) from 1.13 at.% to 8.24 at.% (Table 1, entry 2, 3, 4). Benzene-CNTs (Table 1, entry 5) and blank electrocatalyst (Table 1, entry 6) were also prepared under similar reaction conditions. Notably, the N was not detected from the blank electrocatalyst, indicating that no pyridine was present in the sample and that the unreacted pyridyne precursor can be removed from the crude reaction material using current procedures.

The XPS core spectra of C1s and N1s were deconvoluted to study the surface chemistry of the prepared samples. The C1s spectra of pristine CNTs (Figure S1,1a, Supporting Information) showed predominately C–C sp^2 peak (≈ 284.8 eV), with a small C–C sp^3 (≈ 285.6 eV) due to minor edge defects; the peaks at 286.6 eV, 287.5 eV, and 290.9 eV were assigned to the C–O, C = O and π – π transition.^[19] Compared with the pristine CNTs, the C–C sp^3 peak of the pyridine functionalized samples significantly increased (Figure 1(1a,2a,3a)) as contributed by the formation of new C–C sp^3 bonds during cycloaddition reaction between the pyridyne intermediates and the CNTs surface, which is demonstrated in the reaction of Scheme 1; moreover, the newly emerged peak at ≈ 286.3 eV were attributed to the C–N sp^2 bond originated from the pyridine aromatic ring. Notably, a carbonate peak (≈ 288.8 eV) was observed in the 8.24% NCNTs (Figure 1(3a)) due to increased oxygen affinity of the highly functionalized samples. As shown in Figure S1,2a (Supporting Information), the C–C sp^3 peak for benzene-CNTs slightly increased compared with that of pristine CNTs as contributed by the formation of new C–C sp^3 bond between the benzene molecule and the CNTs, which is similar to the pyridine functionalization process as demonstrated in Scheme S1 (Supporting Information), indicating successful functionalization of benzyne with CNTs. For blank catalyst, no clearly increase of the C–C sp^3 peak was observed and the C–N sp^2 peak was not shown in the C1s spectra (Figure S1,3a, Supporting Information), suggesting no pyridine functionalization occurs on the blank catalyst.

For the N1s spectra (Figure 1(1b,2b,3b)) the pyridinic N peak appeared at ≈ 399.5 eV, which has positively shifted by 0.5 eV – 0.8 eV compared with previous research.^[8a] The discrepancy of pyridinic N binding energy is possible because that the unique structure of the “external” pyridine sites composed of different conjugation with the π system of CNTs.^[14] The unexpected peak around 401.5 eV is possibly due to the contamination by the moisture from the air, in which case, either the N atoms were protonated or the C atoms adjacent to the N atoms adsorbed

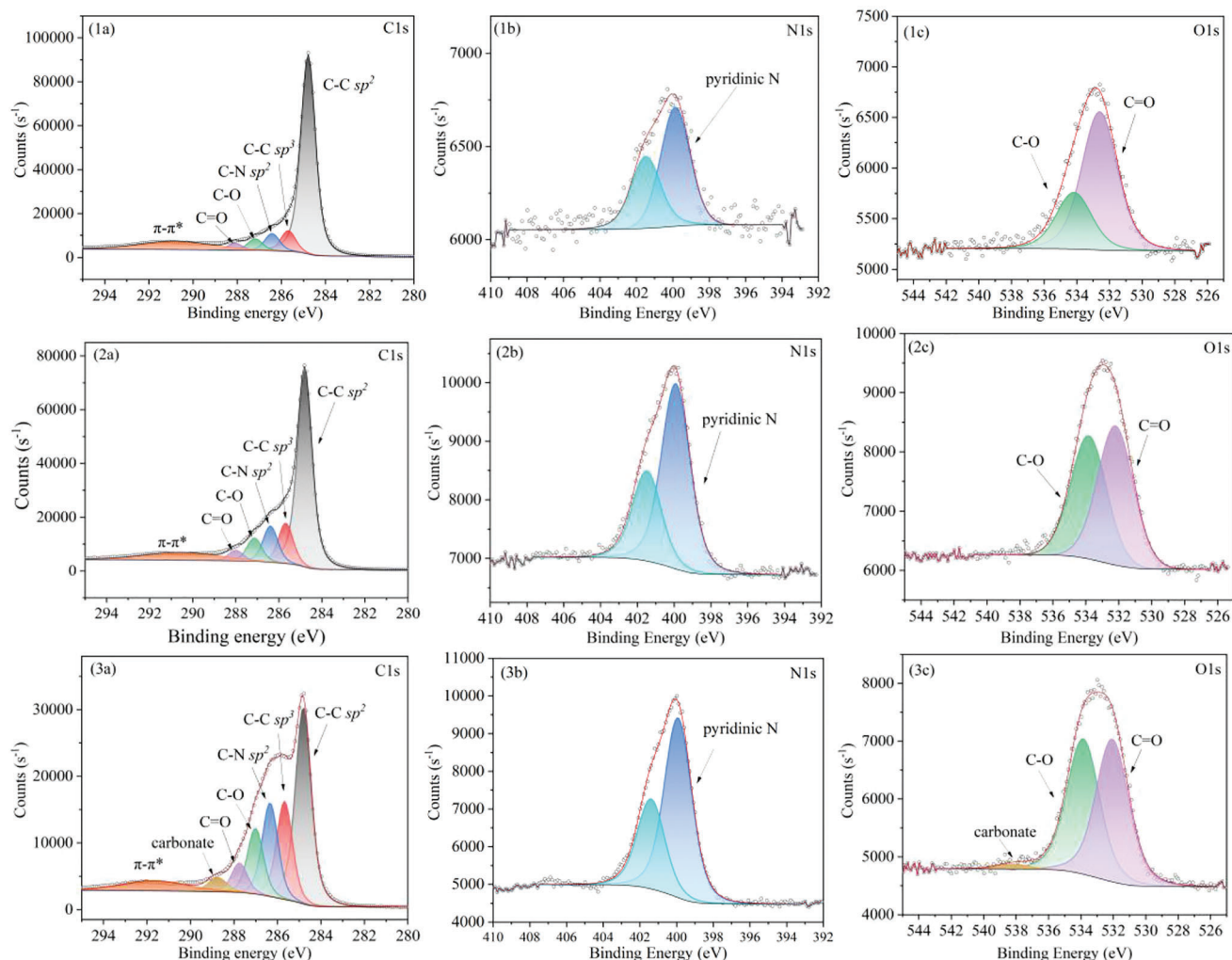


Figure 1. XPS core spectra of C1s (1a), N1s (1b), and O1s (1c) for the 1.13% NCNTs; the C1s (2a), N1s (2b), and O1s (2c) for the 3.78% NCNTs; the C1s (3a), N1s (3b), and O1s (3c) for the 8.24% NCNTs.

hydroxyl groups.^[20] Further work on DFT modeling in this research demonstrated that this contamination of the N is more favored by the protonation of pyridinic N sites to form the pyridinium N sites. Moreover, the absence of peaks corresponding to pyrrolic N and graphitic N in the N1s core spectra reinforces the exclusively incorporation of pyridinic N structures into the CNTs. Further analysis of the O environment from the O1s spectra (Figure 1(1c,2c,3c)), C=O (≈ 532.2 eV) and C—O (≈ 533.7 eV) peaks can be deconvoluted for both samples; carbonate peak (≈ 538.2 eV) can be observed from 8.24% NCNTs (Figure 1(3c)), which shows good agreement with the C1s results.

Notably, the XPS technology is limited to surface analysis with a depth resolution of ≈ 10 nm, and therefore, thermogravimetric analysis (TGA) was employed to further investigate the functional degree of the prepared samples. The TGA curves presented in Figure 2a indicated that the functionalized samples experienced weight loss upon heating to 100 °C, which was possibly attributed to the desorption of moisture adsorbed from the air. A steep decrease in weight was then observed between 250 and 600 °C as assigned to the decomposition of the functionalized

pyridine moieties on the CNTs.^[13] To investigate the desorption behavior of pyridine molecules, pyridine was physically adsorbed on the CNTs (py@CNTs) and analyzed by TGA. As demonstrated in Figure 2a, the TGA curve for py@CNTs exhibited a weight loss between 50 and 115 °C, which was attributed to the desorption of pyridine molecules. Notably, due to the highly volatile nature of pyridine and its weak π - π interaction with CNTs, only a negligible 0.52% weight loss of pyridine was observed. In addition, the TGA curves of 3,4-pyridyne precursor (Figure S2, Supporting Information) suggested that the decomposition occurred between 68 and 130 °C. Based on the above results, it can be concluded that any pyridine and 3,4-pyridyne precursor have been effectively purified from the covalently functionalized pyri-CNTs. Upon heating to 1000 °C, the weight loss for pristine CNTs was only 1.23%, indicating high purity of the CNTs; while for the functionalized samples, the weight loss was 4.10%, 12.7%, and 28.7% for the 1.13% NCNTs, 3.78% NCNTs, and 8.24% NCNTs, respectively. The functional degree was further calculated based on the TGA weight loss, which is defined as one pyridine molecule per unit number of carbon atoms of the CNTs.^[13] As shown in Table S1

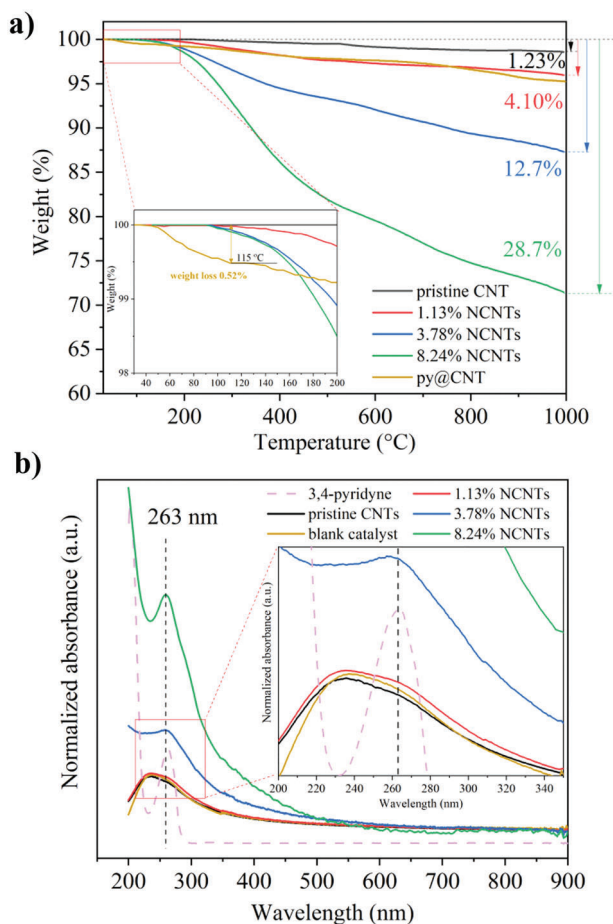


Figure 2. a) TGA curves of prepared samples, the inserted graph shows the enlarged TGA curves from room temperature to 200 °C; b) UV-vis spectra of 3,4-pyridine precursor and prepared samples, the inserted graph shows the characteristic peak area near 263 nm.

(Supporting Information), the functional degree was 1/150 (i.e., 1 pyridine per 150 C atoms) for the 1.13% NCNTs, 1/44 for the 3.78%, and 1/16 for the 8.24% NCNTs. Furthermore, elemental analysis was performed to confirm the N content of the samples, and the detected N content was 0.54 wt.%, 2.28 wt.%, and 5.26 wt.% for the 1.13% NCNTs, 3.78% NCNTs, and 8.24% NCNTs, respectively. The characterized N content based on the TGA and the elemental analysis were both in good consistent with the atomic percentage from the XPS results.

Ultraviolet-visible spectroscopy (UV-vis) provides information on the presence of pyridine. As shown in Figure 2b, a strong characteristic peak appeared at 263 nm in the spectrum of 3,4-pyridine precursor. The spectra of pristine CNTs and blank electrocatalyst were nearly identical (Figure 2b, inserted figure), indicating that pyridine molecules were not detected in the samples. This finding further confirms the successful removal of unreacted pyridine precursors from the sample. The characteristic peak of pyridine precursor can be noticed on the spectra of 1.13% NCNTs and became more pronounced in the spectra of the 3.78% NCNTs and 8.24% NCNTs. The gradual appearance of the pyridine characteristic peak agrees well with the increasing functional degree of the samples. The observations from UV-vis together with

the XPS and TGA results strongly support that the pyridine rings were covalently functionalized on the surface of the CNTs.

2.2. Defects and Electronic Structures

Pyridine cycloaddition forms two covalent C—C sp^3 bonds between each pyridine ring and the CNTs, and therefore alters the sp^2 conjugation of the CNTs outer layer, as demonstrated in Scheme S2 (Supporting Information). Raman spectroscopy was employed to assess the disorder and defective structures in the CNTs. In the Raman spectra of CNTs, the D band ($\approx 1330\text{ cm}^{-1}$) stands for the defective structures, and the G band ($\approx 1570\text{ cm}^{-1}$) refers to the C—C sp^2 structure of the well-defined graphene plane, while the D' band ($\approx 1630\text{ cm}^{-1}$) may occur in some cases contributed by the double resonance of the defects in the nano crystalline structures.^[21] Additionally, the ratio of D band and G band intensity (I_D/I_G) provides a direct evaluation on the degree of defects in the structures.^[13] The samples with a higher functional degree displayed increased intensity and broadening of both the D band and D' band (Figure 3a), signifying augmented structural defects in the sample. Furthermore, the I_D/I_G value increased from 0.219 for pristine CNTs to 0.235, 0.319, and 1.705 for the 1.13% NCNTs, 3.78% NCNTs, and the 8.24% NCNTs, respectively. The boosted I_D/I_G value further confirms increased defects in the highly functionalized samples, as attributed to the formation of covalent bonds between pyridine and the CNTs surface could disrupt the well-defined sp^2 C structures.

To investigate the impact of covalent functionalization on the electronic structures of the CNTs, Ultraviolet Photon Spectroscopy (UPS) was utilized to calculate the work function, which provides evidence of the electron-donating capability of the catalyst. As shown in Figure 3b, the measured work function for pristine CNTs was 4.23 eV, which agrees with the reported value of multi-walled CNTs measured by UPS.^[22] and the work function gradually decreased to 4.16 eV, 4.05 eV, and 3.94 eV for 1.13% NCNTs, 3.78% NCNTs, and 8.24% NCNTs. In the case of ORR electrocatalysts, the lower work function is generally related to higher ORR activity by facilitated interfacial charge transfer with the adsorbed oxygen.^[9b,23] It is therefore likely that the structural defects created by the covalent bonds can, to some extent, improve the ORR reactivity by enhancing the electron-donating capability of the samples. Furthermore, 4-probe was used to investigate the electron mobility within the samples. As shown in Figure 3c, the pristine CNTs are highly conductive with a measured electrical resistance of only 0.004 Ω . After functionalization, the electrical resistance increased to 0.127 Ω for 1.13% NCNTs, 0.241 Ω for 3.78% NCNTs, and boosted to 1.242 Ω for 8.24% NCNTs. The increased electrical resistance of the functionalized samples can be attributed to the functionalized pyridine rings, which are electrical resistive.

2.3. Morphologies and Microstructures

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the morphologies and microstructures of the samples. The SEM image of pristine CNTs (Figure 4a) presented a spaghetti-like shape, and clean

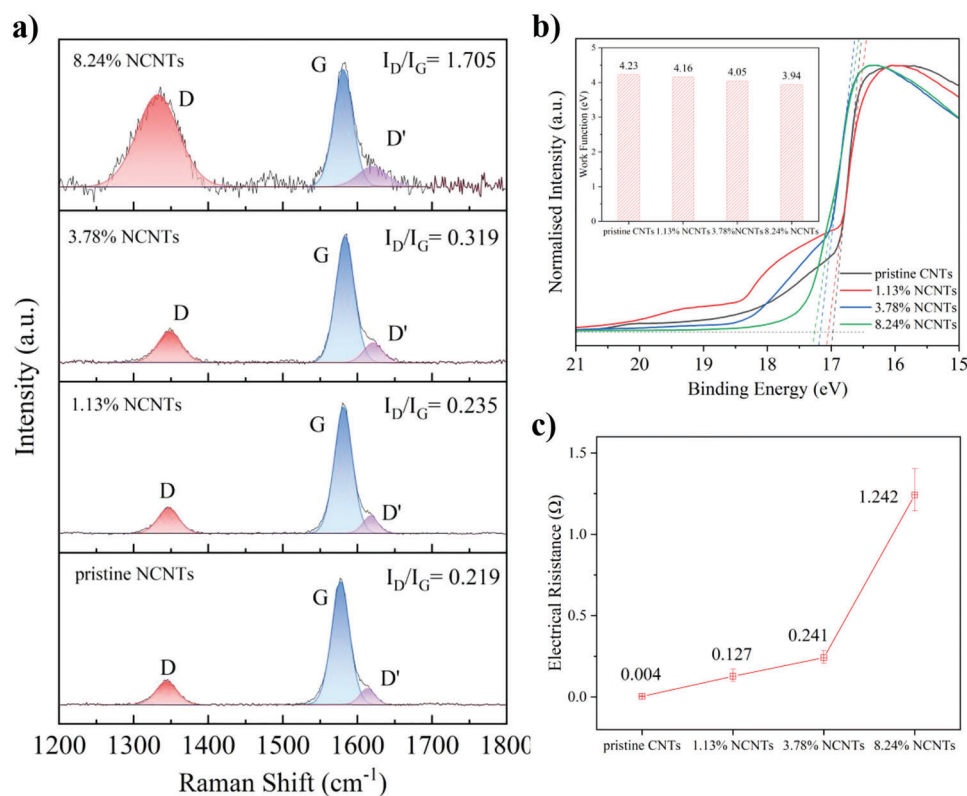


Figure 3. a) Raman spectra of as-prepared samples; b) the UPS secondary electron cut-off edge and calculated work function (inserted graph) of the prepared samples; c) electrical resistance of the samples measured by 4-probe measurement.

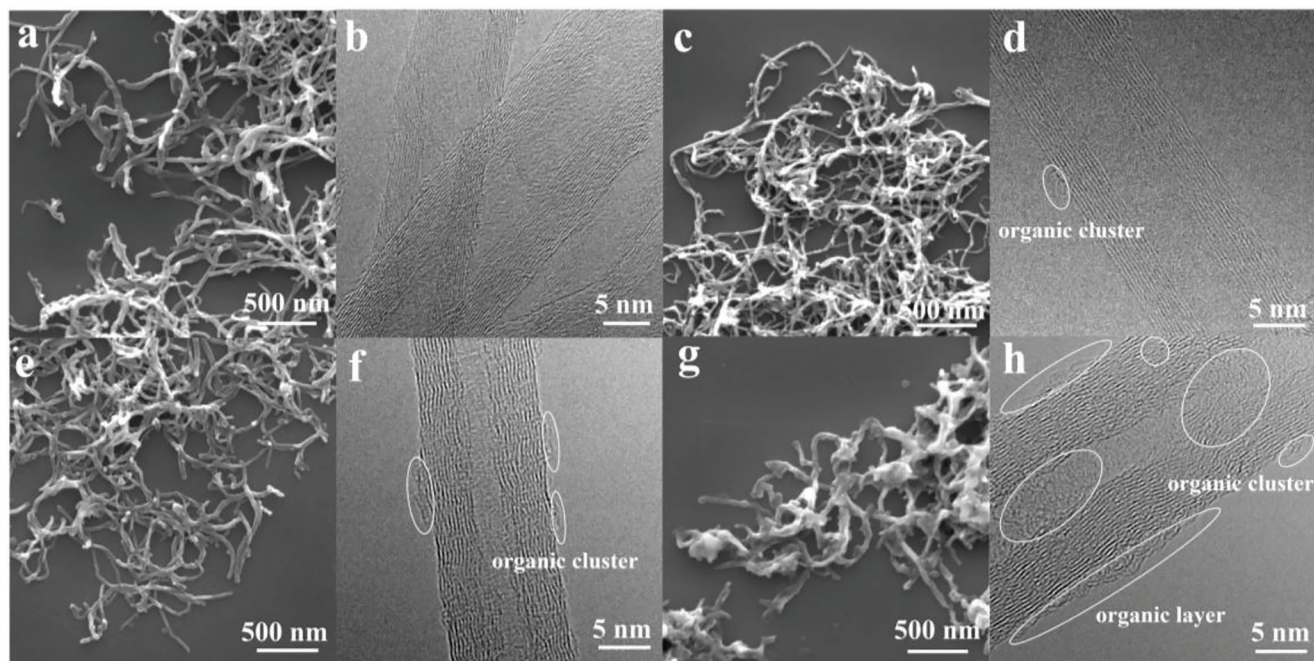


Figure 4. Structural characterization of pristine CNTs and pyridine functionalized CNTs: SEM image (a) and TEM image (b) of pristine CNTs; SEM image (c) and TEM image (d) of 1.13% NCNTs; SEM image (e) and TEM image (f) of 3.78% NCNTs; SEM image (g) and TEM image (h) of 8.24% NCNTs. The organic clusters / layers were circled in the TEM images.

smooth surface as indicated by the TEM image (Figure 4b). After reaction with pyridyne, the CNTs structure was maintained (Figure 4c–h), signifying good tolerance of the CNTs to the functionalization process under heating condition. However, for the 8.24% NCNTs, the surface was coated by thick organic clusters according to the SEM image (Figure 4g). Further observation from the TEM images revealed the presence of small clusters on the surface of 1.13% NCNTs (Figure 4d) and the 3.78% NCNTs (Figure 4f), while more conspicuous organic clusters were observed on the 8.24% NCNTs (Figure 4h). These unexpected organic clusters are likely attributed to the polymerization of pyridines to form aggregates on the surface of the CNTs, which is unavoidable in highly functionalized samples.

Energy dispersive spectroscopy (EDS) mapping was employed to investigate the dispersity of pyridine molecules on the CNTs. The EDS mapping of both samples (Figure S3, Supporting Information) suggested that the N element (yellow dot) appeared homogeneously on the surface of all functionalized samples, indicating good dispersity of the pyridine on the CNTs surface. Notably, weak signals were observed in the EDS mapping of the N element for the pristine CNTs (Figure S3a, Supporting Information) that should not contain any N element, as possibly attributed to the artefacts of the EDS mapping technique.^[24] In addition, the EDS mapping revealed the presence of adsorbed O elements originating from the atmosphere, which is consistent with the findings from the XPS analysis. It can be concluded that the pyridine molecules were evenly dispersed on the CNTs surface, however, aggregation of the pyridine molecules occurs in the highly functionalized samples. As evidenced from the blank CNTs, where most physically adsorbed pyridines were efficiently washed off, the aggregation is likely formed by the polymerization of pyridyne intermediates with existing functionalized pyridine ring via covalent bond (as demonstrated in Scheme S3). In addition, the aggregation of pyridine on arylene / pyridyne functionalized carbon materials has not been recognized in related research as this is the first time such a high functional degree was achieved.

The porosity of the prepared samples was evaluated by N₂-adsorption / desorption isotherms. As shown in Figure 5a, the N₂-adsorption / desorption isotherms showed the IV type isotherm with an H3 hysteresis loop (IUPAC) at higher relative pressure, suggesting analogous mesoporous structures of both pristine CNTs and pyridine functionalized CNTs.^[25] However, the

adsorption volume in the isotherms of both 3.78% NCNTs and 8.24% NCNTs are slightly lower than that of pristine CNTs and 1.13% NCNTs, indicating lower N₂ adsorption capability. As plotted in Figure 5b, the specific surface area increased from 107.66 m² g^{−1} for pristine CNTs to 117.14 m² g^{−1} for the 1.13% NCNTs, possibly contributed by the surface roughness induced by pyridine functionalization. However, with higher functional degree, the specific surface area decreased to 97.01 m² g^{−1} for 3.78% NCNTs and further to 90.46 m² g^{−1} for 8.24% NCNTs. As for the pore size distribution (Figure 5c), higher volume of micropores and less mesopores were identified with an increased functional degree. These results align with the SEM and TEM observations revealing the presence of organic clusters coating the CNTs surface and occupying the pore space, and consequently, the specific surface area was reduced and mesopores were turned into micropores.

2.4. ORR Electrochemistry

The ORR electrochemistry of the pristine CNTs, pyridine functionalized CNTs and benchmark catalyst 20% Pt/C were investigated in 0.1 M KOH electrolyte. In the presence of O₂, the cyclic voltammetry (CV) shows an obvious oxygen reduction peak at ≈0.6 V for all samples (Figure 6a). While the ORR peak of 20% Pt/C catalyst appeared at ≈0.81 V, indicating excellent catalytic activity. As comparison, the background CV curves suggested no reaction on the pristine and pyridine functionalized CNTs in N₂ saturated electrolyte (Figure S4, Supporting Information)

As the ORR reaction pathway is highly dependent on the active sites and microstructures of the catalyst,^[26] the samples were carefully evaluated using a rotating ring disk electrode (RRDE) to investigate the ORR reaction pathway in O₂ saturated 0.1 M KOH electrolyte (Figure 6b). According to the disk current of the polarized curves, pristine CNTs showed relatively poor ORR catalytic activity, and the 1.13% NCNTs clearly promoted the ORR activity. Upon further increase in the degree of pyridine functionalization (3.78% NCNTs and 8.24% NCNTs), the ORR performance became more sluggish compared to 1.13% NCNTs. As a reference, both the pristine CNTs and pyridine functionalized CNTs exhibited significantly lower ORR catalytic activity compared with the 20% Pt/C catalyst. To deconvolute the underlying

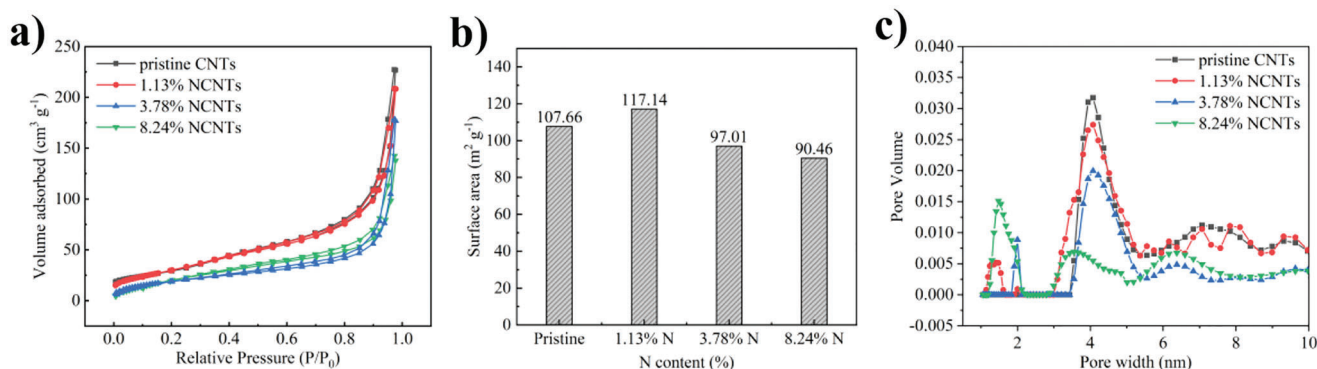


Figure 5. Porosity of prepared samples: a) N₂-adsorption isotherms; b) specific surface area; c) pore size distribution.

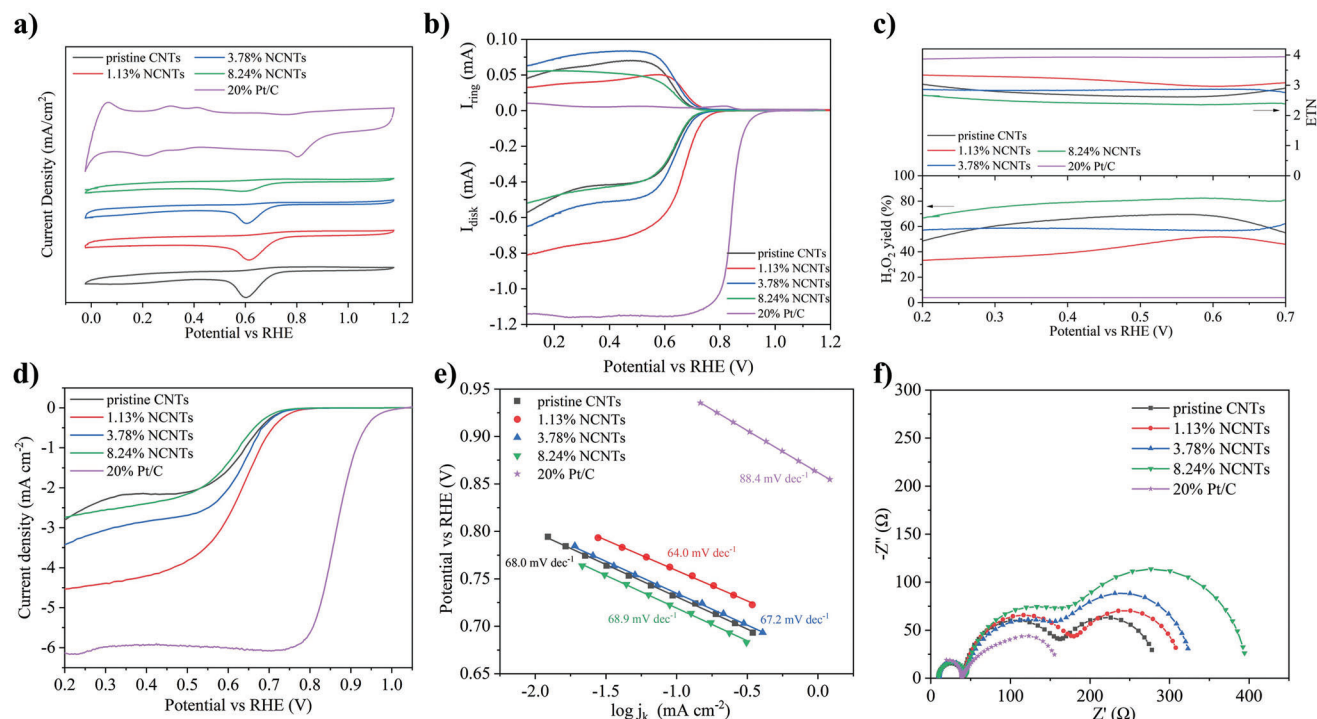


Figure 6. Electrochemistry of as-prepared samples. a) CV curves recorded on RDE in O₂ saturated 0.1 M KOH at scan rate of 100 mV s⁻¹. b) Polarized curves on RRDE recorded in O₂ saturated 0.1 M KOH electrolyte at rotation speed of 1600 rpm and scan rate of 10 mV s⁻¹. c) Electron transfer number (ETN) and hydrogen peroxide yield calculated from the RRDE ring current and disk current. d) LSV recorded on the RDE in O₂ saturated 0.1 M KOH with rotation speed of 1600 rpm and scan rate of 10 mV s⁻¹. e) Tafel slope derived from the LSV curves. f) Fitted Nyquist plots at halfwave potential in O₂ saturated 0.1 M electrolyte with rotation speed of 1600 rpm. The background current in N₂ saturated electrolyte was subtracted and iR drop was compensated for the polarized curves.

reaction mechanisms, the electron transfer number and H₂O₂ yield were calculated accordingly, as shown in Figure 6c. The 20% Pt/C catalyst showed a standard 4-electron pathway and low production of H₂O₂ intermediate. The calculated electron transfer number was between 2–4 in the potential window of 0.7 V to 0.2 V for both pristine CNTs and pyridine functionalized CNTs. More specifically, at the potential of 0.5 V (vs RHE), the electron transfer number of pristine CNTs was close to 2.6, suggesting a 2-electron dominated pathway. In the case of 1.13% NCNTs, the electron transfer number slightly increased to 3.1 at 0.5 V (vs RHE), then dropped to 2.8 for the 3.78% NCNTs and further to 2.5 for the 8.24% NCNTs. Moreover, the H₂O₂ yield for pristine CNTs at 0.5 V (vs RHE) was 68.9%, which dropped to 45.6% for the 1.13% NCNTs and then boosted to 57.7% for 3.78% NCNT and 80.6% for the 8.24% NCNTs, suggesting a predominant 2-electron reaction pathway. These results revealed that although the presence of pyridinic N sites may contribute to the promotion of the 4-electron reaction pathway, the overall ORR process on the pyridine-functionalized catalysts is predominantly governed by a 2-electron pathway. Moreover, the comprehensive characterization of the samples has revealed several detrimental effects associated with higher functionalization levels, including higher electrical resistance, reduced specific surface area, and smaller pore-size structure. These negative factors significantly hamper the catalytic activity of the pyridine-functionalized CNTs toward ORR, consequently favoring the more sluggish 2-electron reaction pathway.

The Linear Sweep Voltammetry (LSV) was further recorded on a rotating disk electrode (RDE) to understand the ORR activity of the catalysts (Figure 6d). The pristine CNTs exhibited rather poor ORR catalytic activity with an onset potential of 0.730 mV and a limiting current density of ≈2.13 mA cm⁻², suggesting that despite the low level of defects and trace amount of iron in the pristine CNTs, these factors did not result in pronounced ORR performance. After pyridine functionalization, the onset potential of 1.13% NCNTs positively shifted by 30 mV from 0.730 mV, and limiting current density nearly doubled from 2.13 to 4.01 mA cm⁻² compared with pristine CNTs, suggesting boosted ORR activity. Compared with the 1.13% NCNTs, the onset potential negatively shifted by 26 mV for the 3.78% NCNTs and further decreased by 14 mV for the 8.24% NCNTs; similarly, the limiting current density dropped to 2.57 mA cm⁻² for 3.78% NCNTs and further to 2.15 mA cm⁻² for the 8.24% NCNTs. The LSV results obtained from RDE measurements are in excellent agreement with the disk current data obtained from the RRDE results. This consistency strongly indicates that the variation in the structure of the catalysts plays a crucial role in the ORR performance by regulating the reaction pathway between the 2-electron and the 4-electron processes.

To highlight the contribution of pyridinic N sites, blank electrocatalyst, and benzene CNTs were evaluated as comparison. As demonstrated in Figure S5 (Supporting Information), the blank electrocatalyst showed similar LSV behavior with the pristine CNTs, which further confirms the successful removal of

residuals and that heating the CNTs with 3,4-pyridine precursor in the reflux procedure without initiating the reaction does not affect the ORR performance and. The onset potential of benzene CNTs was negatively shifted by ≈ 19 mV compared with that of pristine CNTs, which strongly supports the notion that the pyridinic N sites are crucial to promote the ORR activity. Moreover, to investigate the contribution of oxygen groups, the CNTs were intentionally functionalized with ≈ 3.22 at.% of oxygen groups, as determined by XPS analysis (see Experimental Section for the preparation of O-CNTs). The LSV curves for the 3.22% O-CNTs showed a noticeable 33.8 mV negative shift of the onset potential against pristine CNTs (Figure S5, Supporting Information), suggesting that the oxygen groups alone were insufficient to contribute to the ORR process. However, it is worth noting that the oxygen groups may work in cooperation with the nitrogen sites to facilitate the ORR process, as reported by previous research.^[27]

[Tafel slope provides direct index of reaction kinetics, where a lower Tafel slope indicates accelerated ORR kinetics.^[28] As plotted in Figure 6e, the Tafel slopes for all pyridine functionalized CNTs were quite close, indicating similar ORR reaction mechanism, where the initial step of O_2 adsorption was the rate-determining step. The Tafel slope decreased from 68.0 mV dec⁻¹ for pristine to 64 mV dec⁻¹ for 1.13% NCNTs, revealing accelerated kinetics; then the Tafel slope increased to 67.2 mV dec⁻¹ for the 3.78% NCNTs, and further to 68.9 mV dec⁻¹ for the 8.24% CNTs, suggesting suppressed kinetics for the more highly functionalized materials. The Tafel slope of the 20% Pt/C was 88.4 mV dec⁻¹, as attributed to a different reaction mechanism where the rate-determining step was the initial electron transfer to molecular oxygen.^[28,29]

Electrochemical impedance spectroscopy (EIS) was recorded at the mixed diffusion region near the halfwave potential to investigate the electrochemical process at the catalyst-electrolyte interface. The Nyquist plot (Figure 6f), bode plot (Figure S6, Supporting Information) and the equivalent circuit (Figure S15a, Supporting Information) both suggested a similar double-layer capacitance behavior for pristine CNTs and pyridine functionalized CNTs. More specifically, both samples show similar resistance at the high-frequency region (R1), which is controlled by the electron transfer process, suggesting similar electron-donating capability of the catalysts. The semicircle in the medium frequency region on the Nyquist plot was assigned to the capacitive resistance of the double-layers. For the lower frequency region, which is attributed to the mass transfer, the resistance (R3) increased from 122.2 Ω of pristine CNTs to 132.8 Ω , 153.6 Ω , and 220.6 Ω for the 1.13%, 3.78%, and 8.24% NCNTs, respectively (Table S2, Supporting Information). The significant increase in resistance at lower frequency region for highly functional catalyst is possibly due to the reduced surface area and pore diameters that prohibited the mass transfer process. In addition, the resistive organic clusters in higher functionalized samples may contribute to the resistance. The impedance of the 20% Pt/C catalyst was clearly lower than the pristine CNTs and pyri-NCNTs, and the equivalent circuit was slightly different with a Warburg impedance at the higher frequency (Figure S15b, Supporting Information).

Electrochemical surface area (ECSA) is another critical parameter for evaluating the electrocatalysts. The ECSA of the pre-

pared samples was estimated by the double-layer capacitance (C_{dl}) (Figure S7, Supporting Information), and the specific ECSA values were then calculated accordingly (Table S3, Supporting Information). For pristine CNTs, the ECSA was 0.0053 cm² and increased to 0.0239 cm² for 1.13% NCNTs, then the ECSA dropped to 0.0085 cm² for the 3.78% CNTs and to 0.0008 cm² for the 8.24% NCNTs. The trend of ECSA for the prepared samples was consistent with the results from N_2 -adsorption/desorption results and is highly related to the changes in ORR catalytic activity. Therefore, it can be presumed that the reduction of specific surface area and ECSA plays a key role in the suppression of ORR performance for the 3.78% NCNTs and 8.24% NCNTs.

Chronoamperometry was recorded to evaluate the stability of pyridine functionalized CNTs. As demonstrated in Figure S8 (Supporting Information), after running 10 000 s at the halfwave potential, nearly 75% of the current was retained for the pristine CNTs, while only 50% of the current was retained for the 1.13% NCNTs. For the higher level of pyridinic N functionalized samples, the current retention was 63% for the 3.78% NCNTs and 70% for the 8.24% NCNTs. Notably, the chronoamperometric test suggested that the 3.78% NCNTs and 8.24% NCNTs are more stable compared with the 20% Pt/C catalyst. To investigate the changes on the N active sites, the electrocatalysts were recycled after the chronoamperometric test and were characterized on the XPS. As shown in Figure S10a (Supporting Information), the XPS indicated that the N sites were cleaved during the chronoamperometric process, with only 0.02%, 0.63%, and 1.56% of N sites detected for the recycled 1.13% NCNTs, 3.78% NCNTs and 8.24% NCNTs, respectively. Notably, the remaining level of N sites of each sample was in good agreement with their corresponding current retention from the chronoamperometric test. Furthermore, the pyridinic N and pyridinium N can be deconvoluted from the N1s core spectra of the recycled electrocatalyst, which is in good consistence with the N1s spectra of the fresh electrocatalyst.

Accelerated stress test (AST) was performed to further understand the durability of the prepared catalysts. As shown in Figure S9, the pristine CNTs and 1.13% NCNT clearly suffered more from degradation, with the onset potential negatively shifted by 33 mV and 28 mV respectively, and limiting current density reduced by 0.57 mA cm⁻² and 0.8 mA cm⁻² after the AST. While the 3.78% NCNT and 8.24% NCNT showed less severe degradation, with only 11 mV and 7 mV negative shift in the onset potentials, and the reduction of limiting current density was 0.34 mA cm⁻² and 0.05 mA cm⁻² after the AST. It was noted that the pyridine functionalized CNTs, particularly highly functionalized CNTs, showed better durability compared with the 20% Pt/C catalyst, where a 42 mV negative shift in onset potential was observed. The XPS characterization of recycled catalysts suggested only 0.23% of N sites were preserved in the 1.13% NCNTs after the AST, while 2.53% and 5.36% of N sites remained in the 3.78% NCNTs and 8.24% NCNTs (Figure S10b, Supporting Information). The reduction of ORR catalytic activity can be attributed to the cleavage of pyridine molecules during the AST. Another possible reason could be carbon corrosion of the electrocatalyst, which has been extensively reported in the area of carbon-based electrocatalysts for ORR.^[30] Notably, the LSV curves for the 8.24% NCNTs were almost identical before and after the AST test, which

is possibly due to the pyridine aggregates (or large particles) coating the bulk CNT, therefore protecting the samples from carbon corrosion during the AST.

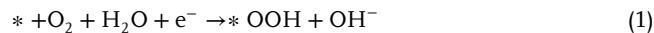
Methanol tolerance (Figure S11, Supporting Information) for both pristine CNTs and pyridine functionalized samples was quite poor, with a significant drop of nearly 20% in current after methanol injection. Among the evaluated catalysts, pristine CNTs exhibited slightly better methanol tolerance followed by the 8.24% NCNTs and 3.78% NCNTs, while the 1.13% NCNTs showed more current loss. Notably, the Pt/C catalyst suffered the most severe current loss after methanol injection, indicating a much poorer methanol tolerance compared to the prepared NCNTs.

To verify the reproducibility of the conclusions on the ORR catalytic reactivity, another series of samples were prepared using the same procedures and reaction conditions as listed in Table 1, and the ORR performance of the reproduced samples was found to be in accordance with the previous data (Figure S12, Supporting Information). Similar to the results above, the LSV of the catalyst also shows suppressed ORR activity with higher degree of pyridine functionalization. With particular interest, the ORR behavior of the prepared samples was investigated in 0.1 M HClO₄ electrolyte. As shown in the LSV curves (Figure S13, Supporting Information), the ORR catalytic activity was profoundly improved for the 1.13% NCNTs compared to the pristine CNTs, and with more pyridine functionalized on the CNTs, the ORR catalytic activity was suppressed for the 3.78% NCNTs and the 8.24% NCNTs. The ORR behavior in the acidic electrolyte is in excellent agreement with that in the alkaline electrolyte. Overall, it can be concluded that pyridine functionalization can, to some extent, enhance the ORR performance via a 4-electron and 2-electron mixed ORR process. However, higher functionalization level of pyridine introduces several negative effects, favoring the 2-electron process and limiting the overall ORR performance.

2.5. DFT Modeling

DFT modeling was carried out to gain deeper insights into the ORR process on the pyridine functionalized CNTs. As suggested previously by XPS results, an unexpected peak at ≈ 401.5 eV was observed from the N1s spectra. According to the literature, this peak is likely assigned to the pyridinium N or pyridonic N structure which was formed by either protonation of the N atoms or by adsorption of the OH moieties on the neighboring C atoms.^[20] To further verify this justification, the formation of pyridinium N and pyridonic N was studied by calculating the adsorption energy of adsorbed H (H*) on the N atom and adsorbed OH (OH*) on the adjacent carbon atoms. As shown in Figure S14a (Supporting Information), H* protonation on the N atom requires an adsorption energy of 0.227 eV. The calculated adsorption energy for the OH* on the C atoms neighboring the N site were 0.265 eV and 0.582 eV, respectively (Figure S14b,c, Supporting Information), however, the OH* adsorption on the N site was not achieved (Figure S14d, Supporting Information). This result suggested that the formation of the pyridinium N sites was more favored over the pyridonic N sites.

Based on previous research, the 4-electron process on N-doped carbons can be described as follows:



Above all, the O₂ adsorption coupled with the proton from water and electron transfer (step 1) is well-accepted as a crucial step of ORR on the N-doped carbon catalyst. The ORR processes of both pyridine-CNTs (Figure 7a) and pyridinium-CNTs (Figure 7b) were investigated on the corresponding change in Gibbs free energy (ΔG) at each step. In addition, benzene-CNTs (Figure 7c) were also investigated in comparison to the pyridine-CNTs.

For the pyridine-CNTs, the C atoms adjacent to the pyridinic N are the most possible oxygen adsorption sites on the initial step, since these C atoms carry more positive charges attributed to the electronegative N atoms.^[9a,14,31] As shown in Figure 7a, the calculated ΔG was 1.244 eV and 1.347 eV for the C atoms at the P1 and P2 positions neighboring to the pyridinic N, slightly lower than that of benzene-CNTs. For the pyridinium N (Figure 7b), the ΔG of the oxygen adsorption step were -1.135 eV and -0.476 eV on the C atoms at the P1 and P2 positions adjacent to the pyridinium N, which were clearly negative compared to the pyridine sites, revealing pronounced ORR catalytic activity for the pyridinium N sites with a spontaneous exothermic process on the initial step. Nearly 30% of the N sites were pyridinium N in the pyridine functionalized CNT sample, according to the XPS results, due to the contamination from the moisture in the atmosphere. A reasonable hypothesis is that more pyridinium N sites will form in the electrocatalyst during the ORR evaluation once the catalyst was exposed to the aqueous electrolyte. In the case of benzene-CNTs (Figure 7c), the calculated ΔG for oxygen adsorption on the P1 and P2 carbon atoms were 1.504 eV and 1.339 eV, suggesting poor ORR catalytic activity with an endothermic process in the initial step. Therefore, the pyridinic N sites were critical for the ORR process, and the pyridinium N sites, as formed from pyridinic N in an aqueous electrolyte, significantly promoted the ORR performance.

Subsequently, the *OOH species was reduced stepwise to two OH⁻ ions, as demonstrated earlier (step 2–4). The computed energy profile provided further insights on the rate-determining step of the ORR process according to the calculated ΔG values. In the case of both pyridine-CNT (Figure 7a) and benzene-CNT (Figure 7c), the rate-determining step was identified as the oxygen adsorption and protonation step (step 1), as evidenced by larger ΔG values compared to other steps of the reaction on each adsorption site. However, for pyridinium-CNTs, the rate-determining step was the final stage involving the reduction and desorption of *OH species to generate the OH⁻ ion (step 4), which was an endothermic process with ΔG increasing by 0.132 eV and 0.405 eV on the P1 and P2 positions (Figure 7b). This observation can be attributed to the protonation of the N atom, which facilitated the stabilization of the product and led to a higher energy barrier for desorption in the final step. Therefore,

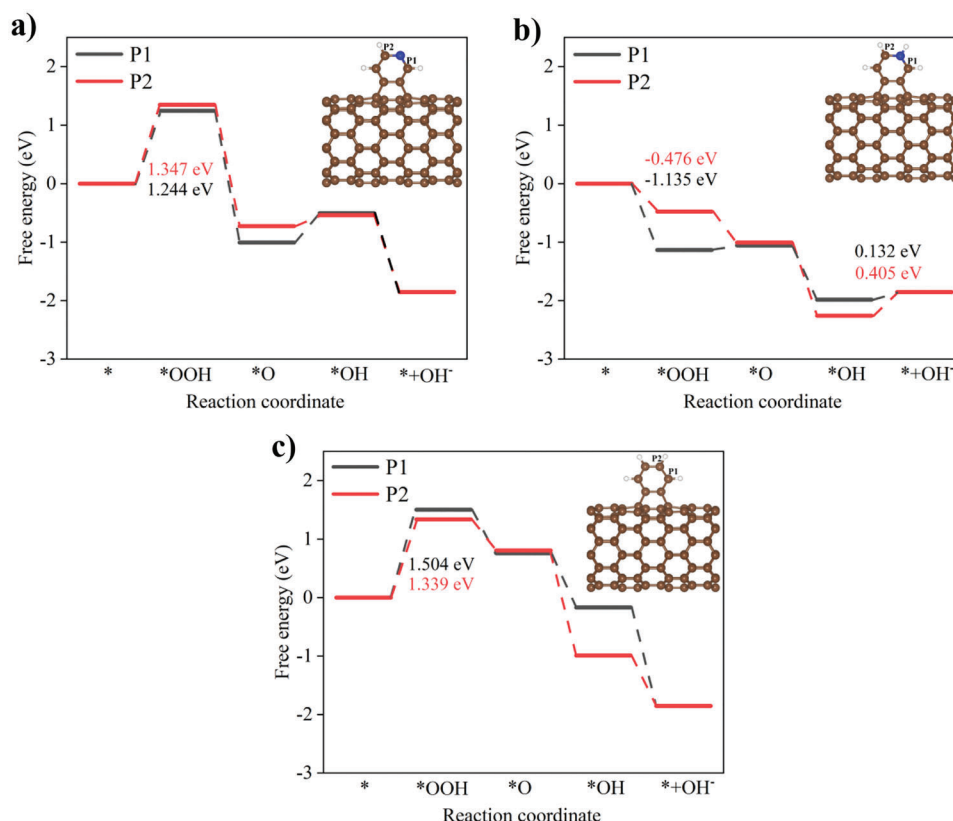


Figure 7. Free energy profile of the ORR process on a) the pyridine-CNTs, b) the pyridinium-CNTs, and c) benzene-CNTs.

the ORR performance on pyridinium-CNTs was significantly improved compared with benzene-CNTs, which is consistent with our experimental results.

3. Conclusions

In summary, a series of exclusively pyridinic nitrogen functionalized CNTs have been prepared via a new and operationally simple pyridyne cycloaddition approach. A higher functional degree was achieved in this work compared with similar research, thus enabling the investigation of the samples with different level of N from low to high. Comprehensive studies on the structure-performance relationships were conducted, as well as DFT modeling for the ORR process. We demonstrated that the covalently functionalized pyridine molecules are the crucial active sites for the ORR process. Furthermore, pyridine aggregation in highly functionalized samples is inevitable, resulting in a series of negative structural effects and leading to higher resistance of mass transfer and charge transfer. Therefore, an optimal degree of functionalization was established, containing sufficient pyridine sites to promote the ORR activity but less influenced by the negative structural effects. This leads to an enhanced ORR process with a 4-electron dominated pathway. Conversely, the more highly functionalized samples suffer more from the negative structural effects, leading to a suppressed ORR process with a 2-electron dominated pathway. To the best of our knowledge, this is the first time that pyridine functionalization has been shown to induce negative structural effect on ORR. DFT calculation revealed that the favored O_2 adsorption sites were the C atoms adja-

cent to the N site, and protonation of the N atoms further assisted the ORR process.

This work achieved rational incorporation of solely pyridinic (and “external”) N sites onto the CNTs as part of a conceptual study to deconvolute the role played by the pyridinic N type within N-doped carbon materials. The detailed structure-activity relationship that is presented in this study will provide valuable guidance for the development of related research in this area. It is noted that while the absolute ORR catalytic performance and durability of the materials were low compared to conventionally prepared electrocatalysts, these were not the principal focus of this study. As such, future research should focus on developing novel strategies to prevent the observed aggregation during the functionalization process and improving the durability of the covalently functionalized catalysts for better electrocatalytic performance in real-world applications. This paper is hoping to provide valuable insights for the design and development of high-performance electrocatalysts for energy applications.

4. Experimental Section

Materials: The 3,4-pyridyne precursor was synthesized according to a well-established procedure^[32] and the details can be found in the supporting information. The chemicals used for the synthesis of the 3,4-pyridyne precursor were purchased from Sigma Aldrich (UK) and were used without purification unless otherwise stated. Benzene precursors were purchased from TCI Ltd., UK. For the functionalization of CNTs, the CNTs (multi-walled, 99.9% purity, OD 15 nm) were purchased from Ossila Ltd and used directly without further treatment. *ortho*-Dichlorobenzene (oDCB)

was purchased from Alfa Aesar (97%) and was dried over activated 4 Å molecular sieves, then purged with N₂ flow for at least 2 h before use. TBAT was purchased from Sigma Aldrich. The PTFE membrane filter was purchased from Sigma Aldrich (Ominipore, hydrophilic, 0.2 µm pore size). For the electrochemical test, ethanol (99.9%) was purchased from Sigma Aldrich (UK). Nafion D-521 (5 wt.%, dispersed in water and 1-propanol) was purchased from Alfa Aesar. Potassium hydroxide hydrate (Sigma Aldrich, 99.995% Suprapur) was used to prepare the KOH electrolyte. For the evaluation in acidic electrolyte, high purity perchloric acid (Honeywell, stoke No. 017-006-00-4) was used to prepare the 0.1 M HClO₄ electrolyte. High-purity oxygen, nitrogen, and hydrogen were purchased from BOC Ltd., UK. Deionized water (18 MΩ cm) was used for all experiments.

Fabrication of Pyridinic NCNTs: The pyridine functionalized CNTs were prepared according to modified literature procedures.^[13b,14] For a typical preparation procedure for the 1.13% NCNTs, to the mixture with pristine CNTs (40 mg) and TBAT (108.0 mg, 0.2 mmol, 2.0 eq.) was added oDCB (10 mL) in a sealed vial under argon, followed by a solution of 3,4-pyridine precursor (29.9 mg, 0.1 mmol, 1.0 eq.) in oDCB (5.0 mL) added dropwise by syringe. The resulting mixture was placed in a bath sonicator (RS PRO, JP-0315) for 15 min in an ice bath before stirring and heating at 80 °C for overnight (15 h). After completion, the resulting suspension was cooled to room temperature and the mixture was then separated by centrifugation. The resulting solid was then filtered using a PTFE membrane and washed thoroughly with 50 mL DMF and 50 mL methanol several times. The solid was collected and dried in vacuo at 60 °C overnight to afford the pyridinic NCNTs (pyri-NCNTs). The details of reagent usage for each sample were listed in Table 1.

Fabrication of Benzene-CNTs and Blank Catalyst: Benzene-CNTs were prepared via the aforementioned procedure for pyridinic CNTs using benzene as the precursor (Scheme S1, Supporting Information). For the purpose of comparison, the blank catalyst was prepared according to the same procedure (above) without adding TBAT reagent, so as to investigate the effects of CNTs without covalent functionalization.

Fabrication of O-CNTs: The oxygen groups functionalized CNTs were prepared by stirring 40 mg CNTs in 15 mL oDCB in open air overnight. The resulting suspension was separated and purified via same procedures as described for the pyri-NCNTs.

Preparation of py@CNTs: To a sealed vial under nitrogen, 10 mg of pyridine was added to 40 mg of CNTs in 10 mL DCM under Argon. The suspension was stirred at 50 °C overnight. After completion, the sample was collected by evaporating the DCM under rotavapor, then placed in air for 5 h to volatile off the remaining DCM to afford the py@CNTs sample.

Characterization: ¹H NMR and ¹³C NMR spectroscopy of synthesized compounds was performed on a Bruker HD 400 MHz spectrometer. ICP-OES was performed on Thermo Fisher ICP-OES-7400. Before analyzing, the commercially purchased CNTs sample was carefully weighed and then digested in 10 mL of aqua regia using a MARS 6 microwave at 1500 W for 20 min. The resulting suspension was filtered, and the solution was diluted to 20 mL for analysis. XPS was performed on a ThermoFisher Nexsa Surface Analysis System using Ka X-ray source. The as-prepared samples were dried under a vacuum at 80 °C overnight before test. The data were calibrated to 284.8 eV for the C 1s peak; the high-resolution spectra were deconvoluted on CasaXPS software, with the FWHM of deconvoluted peaks set as equal. Elemental analysis was performed on the Thermo Flash Elemental Analyser. TGA was performed on Q500 Thermogravimetric Analyzer (TA Instruments, USA). The sample was heated in N₂ flow from room temperature to 1000 °C with a ramp program of 10 °C min⁻¹. Elemental analysis was performed on the Thermo FlashEA 1112 Analyzer, and samples were measured twice to ensure accuracy. UV-vis spectroscopy was recorded on the Agilent Cary 100 (Agilent Technologies, Inc.). For the sample preparation beforehand, all CNTs related samples were first dispersed in SDS solution (Sodium dodecyl sulfate, Sigma Aldrich, 1% w/v aqueous solution) then sonication for 30 min to acquire a clearly dispersed solution, while the 3,4-pyridine precursor was dissolved in ethanol. Raman spectroscopy was recorded on Renishaw inVia Confocal Raman microscope, with a 633 nm laser source. CasaXPS software was used to deconvolute the peaks and to calculate the I_D/I_G ratio. For the four-probe test, the powder sample was loaded on a stainless-steel substrate and

pressed under 1 bar for 5 min to obtain a 1 cm diameter circular tablet; then the as-prepared sample was measured in a four-probe apparatus at room temperature. All samples were tested at least five times to ensure accuracy. SEM was performed on an FEI Inspect-F facility. The SEM sample was prepared by sonicating 1 mg of sample in 1 mL absolute ethanol for 20 min, then drop-casted 10 µL on a silicon wafer and left to dry in air for at least 10 min. TEM and EDS mapping were performed on a JOEL 2100F. The TEM samples were prepared by sonicating 1 mg sample in 1 mL absolute ethanol for 20 min, then drop-casted on a copper TEM grid and left to dry in air for 10 min. For the N₂-adsorption / desorption, the sample was degassed overnight at 120 °C under vacuum. The isotherm was measured on a NOVA 4200 system (Quantachrome Instruments, USA). The specific surface area was calculated by multipoint Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated based on quenched solid density function theory (QSDFT) using the adsorption branch.

Electrochemical Tests: The electrocatalyst ink was prepared by mixing 4.0 mg of the sample with 36 µL Nafion solution (5% w/w), 264 µL ethanol, and 700 µL de-ionized water. The mixture was placed in bath sonicator for 20 min before ultrasonication by probe sonicator (Fisherbrand model 705, US) for 10 min using a 5 s on and 5 s off pulse procedure. The RDE electrode was prepared by drop casting 5 µL of the prepared ink on the pre-polished 3 mm glassy carbon electrode and then dried at room temperature for 1 h at a rotation speed of 700 rpm. For the RRDE electrode, 14 µL of the prepared ink was carefully added onto the pre-polished 5 mm RRDE electrode and then dried at room temperature for 1 h with a rotation speed of 700 rpm. The catalyst loading was ≈0.283 mg cm⁻² for both RDE and RRDE electrodes. The ORR test was performed on an electrochemical potentiostat (Metrohm Autolab PGSTA101) connected with a three-electrode half-cell, consisting of glassy carbon electrode as the working electrode, Pt wire as counter electrode and Hg/HgO as reference electrode. For the measurements in 0.1 M HClO₄ electrolyte, the reference electrode was Ag/AgCl in 3 M KCl solution. The electrolyte was purged for at least 15 min with high purity N₂ or O₂ before test with a flow rate of 80 mL min⁻¹. Prior to measurement, the reference electrode was calibrated over reversible hydrogen electrode (RHE) at room temperature following the recommended procedure.^[33]

The CV, LSV and EIS were performed on the RDE. The CVs were obtained at a scan rate of 10.0 mV s⁻¹; the LSVs were undertaken at a rotation speed of 1600 rpm and a scan rate of 10 mV s⁻¹. The onset potential of LSV was defined as the potential when the current density reaches 0.1 mA cm⁻². Tafel slope was derived from the LSV curves recorded from RDE. The background current in N₂ saturated electrolyte was subtracted and iR drop was compensated. The EIS was recorded at halfwave potential with rotation speed of 1600 rpm. The EIS data fitting was performed on Zview software. For the RRDE test, same condition was used with the ring potential set at 1.5 V (vs RHE) to oxidize the H₂O₂ that was produced during the process. The electron transfer number was calculated according to Equation (5) and the H₂O₂ yield can be obtained from Equation (6):

$$n = \frac{4I_D}{I_D + (I_R/N_c)} \quad (5)$$

$$\text{H}_2\text{O}_2\% = \frac{2I_R/N}{I_D + (I_R/N_c)} \times 100 \quad (6)$$

where N_c is the calculated collection efficiency for this equipment ($N_c = 0.249$ provided by the supplier); I_D is the Faradic current of the disk and I_R refers to the Faradic current at the ring.

ECSA: ECSA was estimated by double-layer capacitance (C_{dl}) calculated from the CV scans recorded in N₂ saturated 0.1 M KOH electrolyte within the non-Faradic region (0.78–0.98 V vs RHE) at different scan rates (20, 40, 60, 80, and 100 mV s⁻¹), and the ECSA was calculated by Equation (7).

$$\text{ECSCA} = \frac{C_{dl}}{C_s} \quad (7)$$

Here, the capacitance current densities $\Delta j / 2$ at 0.88 V vs RHE were measured as a function of the scan rate, and C_{dl} is the fitted slope. C_s is the specific capacitance value of a smooth surface of the material under the specific electrochemical condition. The general value of C_s for the CNT is 0.040 mF cm^{-2} according to previous literatures.^[34]

Stability Test: The chronoamperometric test was performed to understand the stability of the electrocatalysts. The experiment was performed in O_2 saturated 0.1 M KOH electrolyte at the halfwave potential defined by corresponding LSV with a rotating speed of 1600 rpm for 10 000 s. After the chronoamperometric test, the electrocatalysts were collected using a cooper tape before rinsing the electrode in DI water and rotating in the atmosphere, the recycled electrocatalysts were characterized by XPS to understand the changes on N active sites. The AST was performed by running 10 000 CV cycles in N_2 -saturated electrolyte following a well-established protocol by the US Department of Energy (DOE).^[35] The LSV curves were recorded before and after the AST test in O_2 saturated electrolyte. The methanol tolerance test was achieved by injecting 2 M methanol after 200 s during the chronoamperometry test.

Computational Methods: The DFT calculations were performed via the Vienna Ab initio Simulation package (VASP),^[36] and the projector-augmented plane wave (PAW) pseudopotentials were used for the elements involved.^[37] The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) was used to treat the exchange-correlation between electrons.^[38] The involved models are shown in Figure 7 and Figure S14 (Supporting Information). A vacuum region of greater than 15 Å was added around the CNTs to avoid the interaction between periodic supercells. The electron wave function is expanded in plane waves and a cutoff energy of 500 eV is chosen. The Monkhorst-Pack meshes of (1, 1, 5) were adopted for the Brillouin zone (BZ) of the primitive cell.^[39] The convergence in the energy and force was set to be 10^{-4} eV and 0.01 eV Å^{-1} , respectively.

The free energies of $\text{H}_2\text{O}(\text{l})$ and $\text{H}_2(\text{g})$ were used as references when calculating the free energies of reaction intermediates. The adsorption energy for the reaction intermediate is calculated based on Equation (8) as follows:^[40]

$$\Delta G = \Delta E_{\text{Total}} + \Delta E_{\text{ZEP}} - T\Delta S + \Delta G_s \quad (8)$$

where ΔE_{Total} is the calculated adsorption total energy by DFT, ΔE_{ZPE} is zero-point energy, ΔS is entropy, and ΔG_s is solvation energy.^[41]

The calculated ORR electrochemical potential can be obtained as Equation (9):

$$U_L = \text{Mini}[-\Delta G_i] / ne \quad (9)$$

where n is the number of electrons transferred for each electrochemical step, and e is the elementary charge. Here, the n is set to 1 for the one-electron transfer step. The meaning of the r.h.s. of the above equation is to select the smallest $[-\Delta G_i]$ among the ORR elementary steps.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

density functional theory (DFT) modeling, multi-walled carbon nanotubes (MWCNTs), oxygen reduction reaction, pyridinic nitrogen sites, pyridyne cycloaddition

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