Spiral effect of helical carbon nanorods boosting electrocatalysis of oxygen reduction reaction

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ABSTRACT Helical metal-organic frameworks (MOFs) were used as templates or precursors to fabricate helical carbon nanorods (HCNRs) for the first time. Helical carbon contains many topological defects such as pentagonal or heptagonal carbons, which have the potential to facilitate oxygen reduction reactions (ORR). HCNRs show more positive onset/half-wave reduction potentials and higher limited current density than straight carbon nanorods (SCNRs). They also exhibit four-electron oxygen reduction in tests of ORR, while the alternative SCNRs prefer a two-electron reduction mechanism. Experimental and theoretical studies reveal that these enhanced ORR activities can be attributed to pentagon/heptagon defects in HCNRs. This work provides an effective strategy to synthesize helical, defect-rich carbon materials and opens up a new perspective for utilization of a spiral effect for the development of more effective electrocatalysts.

Keywords: helical carbon nanorods, oxygen reduction reaction, spiral effect, pentagon/heptagon defects

INTRODUCTION

Widely existing in nature, the helical structure is an inherent and fascinating feature of chiral macromolecules, such as DNA, proteins and polysaccharides. Biomimetic synthetic helical materials have shown potentials for various applications, including asymmetric catalysts, optical devices and energy storage materials [1–6]. In particular, helical nanostructured materials such as carbon-based helices or metal oxide nanohelices usually show exceptional electrical and optical activities in energy storage and conversion due to their unique morphology, texture and characteristic electrical structures [7–10]. Cobalt-nitrogen co-doped helical carbon nanotubes have been reported as efficient electrocatalysts in oxygen reduction reactions (ORR) because the charges are widely separated by their twisted surface, leading to exposure of more active Co atom sites adsorbed on negatively charged positions [11]. Nevertheless, the use of helical nanomaterials as electrocatalysts has been studied only minimally to date and the effect of helical carbon structure on electrocatalytic performance has not been clarified.

ORR is the key cathode reaction in renewable energy conversion devices such as fuel cells and metal-air batteries [12]. Although Pt-based precious metal materials have been considered as the most efficient electrodes for ORR, their scarcity,

high cost and poor durability limit their commercial applications, and it is therefore important to develop highly efficient, cheap and robust electrocatalysts [13–15]. Since the highly efficient nitrogen-doped carbon ORR electrocatalysts were pioneered by Gong *et al.* [16] in 2009, carbon-based metal-free materials doped with heteroatoms (N, S, P, B) have been widely investigated [17–19]. Heteroatoms could induce charge redistribution to activate neighboring carbon atoms for efficient ORR, and it has been revealed that intrinsic defects, such as zigzag edges, holes and vacancies could produce dopant-free carbons as promising alternatives for efficient electrocatalytic performance [20–22]. Carbon helices with twisted configurations and many defective sites, such as pentagonal/heptagonal carbon rings, have a great potential to facilitate electrocatalysis [23–27]. Thus, the binding energy of oxygen and intermediates can be tuned and optimized by adjusting the helical carbon structure [28–30]. Helical carbons with no doping heteroatoms have not been employed to date as electrocatalysts for ORR. This is because controllable fabrication of helical carbons remains a challenge [31–33], and consequently, the spiral effect on the ORR activity of helical carbons is still unclear.

In recent decades, metal-organic frameworks (MOFs) with large surface areas, long-range ordered structures, and tunable pores have been widely applied in gas storage and separation, and catalysis [34,35]. MOFs are also regarded as distinguished templates or precursors to fabricate porous carbonaceous materials which could inherit the merits of MOFs including their great advantages in uniformly doping heteroatoms, especially single-metal atoms [36,37]. Compared with other precursors, a further advantage of MOFs is that helical structures can be designed and prepared by judicious choice of bridging ligands or strict modulation of synthetic conditions, and will be employed as promising templates to fabricate helical carbon-based materials. To the best of our knowledge, there have been no reports on the use of MOF as a precursor to prepare helical carbonaceous material. This is because it is difficult to synthesize MOFs with mesoscopic helical morphology while retaining the structure of helical MOFs during the pyrolysis process [38–40].

Herein, for the first time, a MOF with mesoscopic helical morphology was employed as a precursor/template in the fabrication of helical carbon nanorods (HCNRs) without doping heteroatoms for ORR (Fig. 1a). After pyrolysis and treatment with acid, the helical MOFs were transformed into HCNRs. For purposes of comparison, straight carbon nanorods (SCNRs)

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Figure 1 (a) Synthetic scheme for the preparation of HCNRs. (b) PXRD patterns of helical MOF nanorods and straight MOF nanorods. (c) SEM image of helical MOF nanorods. (d) SEM image of straight MOF nanorods. (e) PXRD patterns of HCNR-600, HCNR-800 and HCNR-1000. (f) SEM image of HCNR-1000. (g) TEM image of HCNR-1000. Inset: the high-resolution TEM image.

were also prepared by pyrolysis of the non-helical MOF precursor which has the same composition of the helical MOF. Compared with SCNRs, HCNRs exhibit more positive onset/half-wave reduction potentials and higher limited current density. Among the catalysts, the HCNR-1000 is among the best in dopant-free MOF-derived nanocarbon catalysts. Theoretical studies have revealed that the pentagon/heptagon defects in HCNRs play an important role in boosting the ORR activity, and are responsible for catalytic differences between HCNRs and SCNRs.

EXPERIMENTAL SECTION

Synthesis of helical and straight MOF nanorods

The helical MOF nanorods were synthesized using a modified microemulsion procedure [41]. Microemulsion A was prepared by adding 240 μL of an aqueous solution of 1,3,5-benzenetricarboxylic acid trisodium salt (Na_3BTC , 0.1 mol L^{-1}) to 0.05 mol L^{-1} hexadecyl trimethyl ammonium bromide (CTAB) solution in 1.6 mL of 1-hexanol/25 mL of iso-octane. Microemulsion B was prepared by adding 240 μL of an aqueous solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.15 mol L^{-1}) to a 0.05 mol L^{-1} solution of CTAB in 1.6 mL of 1-hexanol/25 mL of iso-octane. The two microemulsions were stirred separately for 30 min at room temperature (RT), and then microemulsion B was dropwise added into microemulsion A. The mixture was stirred further

for 2 h at RT, and the resulting white precipitate was collected, washed with ethanol and deionized water, and dried under vacuum at 70°C for 12 h to afford the helical MOF nanorods. The straight MOF nanorods were synthesized by a similar procedure except that a 0.005 mol L^{-1} CTAB solution was used.

Preparation of HCNR-*T*/SCNR-*T*

In a typical procedure, the as-prepared helical MOF nanorods were heated to 200°C at a rate of 5°C min^{-1} under a nitrogen atmosphere and kept at 200°C for 2 h to remove guest water and organic solvents. The precursor was then heated to the desired pyrolysis temperature (600, 800 or 1000°C) at a rate of 5°C min^{-1} and carbonized for 3 h. After cooling down, the obtained carbon materials were etched with 3 mol L^{-1} HCl solution for one week to remove the residual MnO, then washed with deionized water and dried under vacuum at 70°C overnight to give the final materials HCNR-*T* (*T* represents the pyrolysis temperature). SCNR-*T* was prepared from straight MOF nanorods with the same process.

Physical and chemical characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a Miniflex 600 diffractometer using Cu K α radiation ($\lambda = 0.154 \text{ nm}$). N_2 sorption measurements were performed on a Micromeritics ASAP 2020 instrument. Transmission electron microscopy (TEM) images were taken with an FEIT 20 operating

at 200 kV. Scanning electron microscopy (SEM) images were collected on a JSM6700-F scanning electron microscope. Raman spectra were obtained on a Labram HR800 Evolution instrument over the range of 400–3000 cm^{-1} . X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) using an Al K α source (15 kV, 10 mA).

Electrochemical characterization

A three-electrode system containing a glassy carbon rotating disk electrode as a working electrode, a counter graphite rod electrode and a Hg/HgO/KOH (1 mol L^{-1}) reference electrode was used in all electrochemical measurements. To prepare the working electrode, 1 mg of the catalyst was dispersed in 180 μL of deionized water, 300 μL of isopropyl alcohol, and 20 μL of Nafion binder solution (0.5 wt%) and then sonicated to produce a homogeneous solution. The working electrode was covered with catalyst ink and the mass loading was controlled at 0.2 mg cm^{-2} after drying at RT. Pure Ar or O_2 was constantly bubbled into the electrolytic bath which was filled with 0.1 mol L^{-1} KOH solution. Cyclic voltammetry (CV) curves were recorded in an O_2 /Ar-purged 0.1 mol L^{-1} KOH solution from 0.16 to 1.07 V (*versus* reversible hydrogen electrode (RHE)) at a sweep rate of 30 mV s^{-1} . Rotating disk electrode (RDE) measurements were tested in an O_2 -saturated 0.1 mol L^{-1} KOH solution at potentials from 0.2 to 1.0 V at different rotation rates and with a sweep rate of 5 mV s^{-1} . Rotating ring-disk electrode (RRDE) measurements were conducted under the same conditions as rotating disk electrode (RDE) tests at 1600 r min^{-1} . MeOH stability was assessed with a chronoamperometric method in 3 mol L^{-1} methanol electrolyte, with the potential set at 0.16 V and the rotation speed maintained at 1600 r min^{-1} .

The electron transfer numbers of ORR were determined by RDE according to the Koutecky–Levich (K-L) equations:

$$1/J = 1/J_L + 1/J_K = 1/(B\omega^{1/2}) + 1/J_K, \quad (1)$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6}, \quad (2)$$

where J is the measured current density, J_K and J_L represent the kinetic and diffusion-limiting current densities, respectively, ω is the angular velocity of the disk in the unit of rad s^{-1} , n is the electron transfer number during the ORR, F denotes the Faraday constant (96,485 C mol^{-1}), C_0 is the concentration of O_2 (1.2×10^{-6} mol cm^{-3}) in 0.1 mol L^{-1} KOH, D_0 is the diffusion constant of O_2 (1.9×10^{-5} $\text{cm}^2 \text{s}^{-1}$) and ν represents the kinematic viscosity of the solution ($\nu = 0.01$ $\text{cm}^2 \text{s}^{-1}$ in 0.1 mol L^{-1} KOH).

The electron transfer number can also be calculated through RRDE measurements:

$$n = 4I_d/(I_d + I_r/N). \quad (3)$$

In equation (3), I_r and I_d refer to the current on the ring and disk electrodes, respectively, and N is the collection efficiency (0.442) of the ring electrode.

Density functional theory (DFT) calculations

All structures of intermediates were optimized by the Vienna *Ab initio* Simulation Package (VASP) [42], and were considered with Perdew–Burke–Ernzerh (PBE) flavor of the Projector Augmented Wave (PAW) [43]. The cutoff energy of plane wave basis and the convergence criteria were set to 400 eV and 1×10^{-4} eV, respectively. The k -point sampling of (1,1,1) was adopted.

The noncovalent interactions (NCI), frontier molecular orbi-

als and Mulliken charges were calculated by Gaussian 09 program. The B3LYP hybrid functional in conjunction with the 6-31G(d) basis set was employed in the selected fragment calculations, and the results were further investigated by the Multiwfn package [44].

RESULTS AND DISCUSSION

The helical MOF nanorods, composed of Mn connecting points and trimesic acid (BTC) bridging ligands were synthesized in a CTAB/1-hexanol/iso-octane/water microemulsion at RT [41]. Selective adsorption or desorption of the surfactant CTAB regulates the growth rates of different crystal faces of the MOF, and the decrease of surface free energy may be the driving force for the spontaneous formation of the helical nanorods. The PXRD patterns of the prepared MOF precursors match well with previously reported results (Fig. 1b) [41]. Inductively coupled plasma optical emission spectrometry (ICP-OES) in combination with elemental analysis (EA) confirmed that the molecular formula of the MOF precursors is $\text{Mn}_3(\text{BTC})_2(\text{H}_2\text{O})_6$, containing 24.2 wt% of Mn, 29.8 wt% of C, 3.0 wt% of H and 42.9 wt% of O. Thermogravimetric analysis (TGA) shows that the MOF does not decompose below $\sim 480^\circ\text{C}$ (Fig. S1a). An initial loss of the coordinated water and guest molecules (16.6 wt%) begins at RT and continues to 160°C when a second mass loss emerges due to the partial decomposition of ligands. As displayed in the SEM image (Fig. 1c), the as-synthesized $\text{Mn}_3(\text{BTC})_2(\text{H}_2\text{O})_6$ exhibits a helical morphology with good size uniformity. Based on the statistics of >100 nanorods, the diameters of the helical MOF nanorods are 50–110 nm, their lengths are 0.5–2.0 μm (Fig. S1b) and they have a pitch length of about 130 nm. The circular dichroism (CD) spectrum of the helical MOF shows a significant signal centered at 210–240 nm (Fig. S1c), indicating its ordered chiral structure. Nitrogen sorption measurements revealed a small N_2 uptake and Brunauer–Emmett–Teller (BET) surface area (Fig. S1d), suggesting the low porosity of the helical MOF. For comparison, the straight MOF nanorods were prepared by a similar synthetic procedure. The PXRD patterns of the as-synthesized straight MOF nanorods are consistent with those of the helical MOF nanorods as a result of their identical crystal lattices and composition (Fig. 1b). In addition, the SEM images confirm that the MOFs are straight and rod-like (Fig. 1d). Statistical analysis showed that the diameters of the straight MOF nanorods are typically 60–120 nm and the lengths are 0.5–1.8 μm , similar to the helical MOF nanorods.

The helical MOF nanorods were then employed as precursors and templates to prepare helical carbon nanorods by high-temperature pyrolysis under a N_2 atmosphere. After pyrolysis, the material was treated with hydrochloric acid to remove the residual Mn species. PXRD patterns of the samples before HCl treatment (denoted as HCNRWA, helical carbon nanorods without acid treatment) showed characteristic peaks of MnO (JCPDS No. 06-0592) arising from the decomposition of the MOF precursor (Fig. S1e). After HCl etching, the peaks of MnO disappeared and only two peaks were observed at $\sim 26^\circ$ and $\sim 43^\circ$ (Fig. 1e), which are assigned to the (002) and (101) diffractions of graphite, respectively [45]. ICP-OES indicated that a negligible quantity of Mn remained in HCNRs (Table S1). These results confirm that the Mn species in HCNRs was completely removed after acid etching and would not interfere with the subsequent electrochemical tests. Interestingly, the obtained porous HCNRs, labeled as HCNR- T ($T = 600, 800$, and 1000 for

different pyrolysis temperatures), maintained the helix morphology of the MOF with slightly decreased diameters of 30–100 nm (Fig. 1f and Fig. S1f). TEM images clearly reveal the helical structure of the HCNRs, which is distributed with uniform spiral twists and curved folds (Fig. 1g). The interlayer d -spacing of 0.34 nm in the surface of the HCNRs corresponds to the (002) crystal plane of the graphitic carbon (inset of Fig. 1g) [45]. Prepared from straight MOF nanorods by the same procedure, the SCNR materials show a straight-nanorod morphology and an absence of helical configuration or curved folds with a diameter range of 50–120 nm (Fig. S2). The HCNRs exhibit strong CD signals at 210–240 nm, indicating that the chiral characteristic of the helical MOF precursors has been successfully transformed to the HCNRs, while no obvious signals for the SCNRs emerge (Fig. S3).

We measured the nitrogen sorption isotherms of the carbon materials. The isotherms for HCNRs exhibit a distinct hysteresis loop in the P/P_0 range of 0.5–1.0 (Fig. S4a–c), indicating the existence of mesopores. The pore size distribution, analyzed by non-local DFT (NL-DFT) method further revealed that the HCNRs possess hierarchical porous structures, including micropores (0.3–2 nm) and mesopores (2–40 nm) (Fig. S4d). In addition, the HCNRs show high BET surface areas, with the values changed from 849 m² g^{−1} (600°C) to 254 m² g^{−1} (1000°C), due to the increase of mesopores with the elevated carbonization temperature. The pore volumes of the HCNRs are as high as 0.51–0.68 cm³ g^{−1} (Table S2). The surface area and pore volume of HCNRs are comparable to those of SCNRs derived at the identical carbonization temperature (Fig. S4d and Table S2). The catalysts with hierarchically porous structure, high specific surface areas and large pore volumes could facilitate the exposure of more active sites to electrolyte and oxygen, thus contributing to their boosted catalytic activity.

Raman spectra were used to evaluate the defect degree of the

HCNRs. As shown in Fig. 2a, a G band at ~1580 cm^{−1} is observed, which is attributed to the in-plane stretching mode of graphitic carbon materials, while a D band near 1360 cm^{−1} is associated with defects in graphitic structures [46]. The I_D/I_G ratios of HCNRs are higher with respect to that of the SCNRs derived at the same carbonization temperature (Fig. 2a and Table S3), suggesting that larger numbers of topological defects were generated in HCNRs. To gain a detailed insight into the effect of topological defects on the catalysts, we adopted a two-probe method to measure the electrical conductivities [47]. The HCNRs show higher electrical conductivities (HCNR-1000 ~344.7 S m^{−1}, HCNR-800 ~282.6 S m^{−1}) than the corresponding SCNRs, including SCNR-1000 (~250.2 S m^{−1}) and SCNR-800 (~126.2 S m^{−1}) (Fig. 2b). It has been proposed that electrons in spiral nanocarbons transport with a hopping mode due to the topological defects [9,48]. As a result, with the occurrence of more defects, such as pentagons or heptagons, the HCNRs exhibit higher conductivities. The high electrical conductivities of HCNRs could facilitate the electron transfer process from the catalyst to the adsorbed oxygen.

Fig. 2c, d show the C K-edge X-ray absorption near-edge structure (XANES) spectra normalized to the incident beam intensity of HCNRs and SCNRs. The three characteristic peaks at ~284.0, ~287.1 and ~291.2 eV are assigned to the transition from the C 1s to unoccupied states of C–C π^* , C–H σ^* and C–C σ^* , respectively [49–51]. Theoretical studies have proved that the introduction of pentagons/heptagons (non-sp² hybridized carbon atoms) results in the formation of helical nanocarbons, accompanied by a decrease of the C–C π bondings and an increase in the C–H bondings [23–27]. Interestingly, compared with SCNRs, the absorption intensity of the C 1s $\rightarrow \pi^*$ transition for HCNRs decreases by 4.4% and the C 1s $\rightarrow \sigma^*$ (C–H) transition increases by 10.3% (Table S4). In addition, the XPS analysis further reveals the SCNRs have a strong absorption

Figure 2 (a) Raman spectra of HCNRs and SCNRs. (b) Electrical conductivities of HCNRs and SCNRs. (c) C K-edge XANES spectrum of HCNRs. (d) C K-edge XANES spectrum of SCNRs.

intensity at ~ 284.5 eV, the characteristic of the sp^2 hybridized carbon (Fig. S5), whereas the HCNRs show a weaker signal. These results confirm that the HCNRs possess more pentagonal/heptagonal defects, which agrees well with the analysis of the Raman and electrical conductivities. Importantly, large amount of defects in HCNRs could boost electrocatalysis by providing more rich active sites.

The electrocatalytic O_2 reduction properties of the HCNr and SCNR catalysts were evaluated in O_2 - or Ar-saturated 0.1 mol L^{-1} KOH aqueous solutions with a three-electrode setup. As can be seen in the CV curves, HCNRs show negligible redox response in the Ar-saturated solution (Fig. 3a). HCNRs exhibit well-defined cathodic reduction peaks at $0.68\text{--}0.71 \text{ V}$ vs. RHE in the O_2 -saturated solution, showing significant catalytic reactivity of ORR (Fig. 3b). The linear sweep voltammograms (LSVs) collected by an RDE also demonstrate the high ORR activities of HCNr-600, HCNr-800 and HCNr-1000 (Fig. 3c and Fig. S6). The half-wave potential (0.72 V), limited current density (5.58 mA cm^{-2}) and kinetic current density (21.6 mA cm^{-2} at

0.6 V) achieved by HCNr-1000 are the highest among the as-prepared catalysts, and are almost the best in dopant-free MOF-derived nanocarbon catalysts on record (Fig. 3d and Table S5). In addition, the limited current density of HCNr-1000 is close to that of the commercial Pt/C ($20 \text{ wt\%}$, Alfa Aesar). The high ORR performance of HCNr-1000 is probably due to a synergistic contribution from the large surface area, hierarchical pore structure and high electrical conductivity, as well as high defective site density. Remarkably, the HCNRs surpass the SCNRs derived at the same carbonization temperature in terms of their onset/half-wave potential and limited current density (Fig. 3e and Table S6). The HCNr-1000 shows a half-wave potential of 0.72 V , which is 60 mV more positive than that of SCNR-1000 (0.66 V), and the limited current density reaches 5.58 mA cm^{-2} , while for SCNR-1000 it is only 3.42 mA cm^{-2} . The defective sites in HCNRs play an important role in boosting the ORR activity, and the catalytic deviations between HCNRs and SCNRs are probably due to different proportions of defective sites (pentagons/heptagons) in the materials.

Figure 3 Electrochemical measurements of HCNRs and SCNRs. (a) CV curves of HCNr-1000 in Ar- or O_2 -saturated 0.1 mol L^{-1} KOH aqueous solutions. (b) CV curves of HCNr-600, HCNr-800, HCNr-1000, and $20 \text{ wt\%}$ Pt/C in O_2 -saturated 0.1 mol L^{-1} KOH aqueous solutions. (c) LSVs of HCNr-1000 at various rotation speeds. (d) LSVs of HCNr-600, HCNr-800, HCNr-1000, and $20 \text{ wt\%}$ Pt/C at 1600 r min^{-1} in O_2 -saturated 0.1 mol L^{-1} KOH solution. (e) LSVs of HCNr-600, SCNR-600, HCNr-800, SCNR-800, HCNr-1000 and SCNR-1000 at 1600 r min^{-1} in O_2 -saturated 0.1 mol L^{-1} KOH solution. (f) The electron transfer numbers of HCNRs and SCNRs calculated by the RRDE method. (g) The electron transfer numbers of HCNRs and SCNRs calculated by K–L plots at different voltages. (h) Tafel slopes for HCNRs and SCNRs in an O_2 -saturated 0.1 mol L^{-1} KOH solution. (i) Current versus time (i – t) chronoamperometric responses of the HCNr-1000 and $20 \text{ wt\%}$ Pt/C with rotation rate of 1600 r min^{-1} in O_2 -saturated 0.1 mol L^{-1} KOH, before and after addition of 3 mol L^{-1} methanol.

RRDE measurements were used to further evaluate the ORR performance and mechanism. HCNR-1000 shows an electron transfer number (n) of 3.8–3.7 in a wide potential window of 0.1–0.8 V, implying a dominant four-electron mechanism to reduce O_2 to OH^- directly (Fig. 3f). Meanwhile, SCNR-1000 possesses lower electron transfer numbers, especially at low overpotentials due to its greater tendency to proceed by the inefficient two-electron pathway. The n values of other HCNR catalysts such as HCNR-800 or HCNR-600 are also much higher than those of the corresponding SCNR catalysts (Fig. 3f). The K–L plots that are linear in the potential range of 0.3–0.6 V were also analyzed and the observation matches well with the aforementioned RRDE method, with the n values of HCNRs (~4) surpassing those of SCNRs (~2–3.2) (Fig. 3g). It can be assumed that the spiral effect (the distinct difference between HCNRs and SCNRs) could account for the deviations in the reaction pathways. These results confirm that the spiral effect of HCNRs could not only accelerate the transport of electrons, but also provide abundant active sites for the reduction of O_2 through an efficient four-electron pathway. To learn more about the kinetics of oxygen reduction on HCNRs and SCNRs, the Tafel slopes of the catalysts were calculated from the polarization curves. In the high-polarization region, HCNRs exhibit Tafel slopes of 73.7–95.9 mV dec $^{-1}$ and that increases to >100 mV dec $^{-1}$ for SCNRs (Fig. 3h), indicating the faster ORR kinetics of HCNRs. The methanol crossover effect greatly limits the efficiency and performance of fuel cells, and it is essential to study the fuel tolerance of ORR catalysts. We performed chronoamperometric measurements to test the methanol crossover effect of HCNR-1000 and Pt/C upon the addition of 3 mol L $^{-1}$ methanol solution at 400 s (Fig. 3i). HCNR-1000 is strongly tolerant of methanol crossover effects with a little drop (4.5%) in the ORR current. However, upon the introduction of methanol, an abrupt decrease in current was observed on the Pt/C with a serious current loss of 54.1%.

We further performed several control experiments to explore whether the residual Mn species, if any, could contribute to the

ORR catalytic activity. 2-Methyl-8-quinolinol solution (1 mol L $^{-1}$) was introduced to poison the Mn residue that scarcely exists in HCNR catalysts and the resulting LSVs were nearly identical (Fig. S7a) [52]. We also compared the ORR performance of HCNR-1000 with HCNRWA-1000 before MnO removal. The half-wave potential of HCNR-1000 shifted positively by 20 mV compared with HCNRWA-1000 (Fig. S7b). These findings confirm that the trace amount of residual Mn species is not responsible for the prominent catalytic activity. The observed ORR performance for HCNRs can be exclusively attributed to the intrinsic carbon active sites.

DFT calculations were conducted in an attempt to elucidate the mechanisms of the three structure models, namely C57, C7557 and an ideal graphene layer that were constructed to represent pentagon/heptagon defect sites and non-defective hexagon sites, respectively. As shown in Fig. 4a–c, the pentagon/heptagon carbon atoms in C57 and C7557 models were significantly charged, suggesting the location of electrocatalytic active sites. The assignment of active sites was further affirmed by frontier molecular orbital analysis. The lowest unoccupied molecular orbital (LUMO) is predominantly located at the active carbon atoms and the highest occupied molecular orbital (HOMO) is mainly distributed amongst the neighboring atoms (Figs S8, S9).

We next performed energy analysis on the possible ORR pathways (Figs S10–S12 and Tables S7–S9). Fig. 4d–f show the energetic profiles of two-electron and four-electron ORR pathways on the three models at the equilibrium potential of $U = 1.23$ V vs. RHE. As shown in Fig. 4, the free energy changes of the rate-determining step are lower for C57 and C7557 (0.76 and 0.78 eV, respectively) than for carbons in the hexagons (1.65 eV), consistent with the experimental results that defect-rich HCNRs show higher limiting current and more positive onset/half-wave potentials. The formation of *H_2O_2 and desorption of H_2O_2 in C57 are both thermodynamically uphill with a total free energy change of 0.32 eV. On the contrary, the O–O cleavage pathway from *OOH to $^*O+OH^-$ is exothermic and

Figure 4 Structure models and the calculated atomic charge distributions of (a) C57, (b) C7557 and (c) ideal graphene layer. Energy profiles for different ORR pathways on (d) C57, (e) C7557 and (f) ideal graphene layer.

thus greatly favored (Fig. 4d). Similarly, the formation and desorption of H_2O_2 are also disfavored on C7557 active sites (Fig. 4e). Therefore, it can be concluded that four-electron reduction towards H_2O is the preferred ORR pathway on pentagon/heptagon defect sites. The free energy changes to form $^*\text{H}_2\text{O}_2$ or $^*\text{O}$ intermediates are almost equal on ideal graphene layer, and the desorption of H_2O_2 is thermodynamically more favorable than further reduction to form $^*\text{OH}$ (Fig. 4f). Therefore, it suggests a competing mechanism of two-electron and four-electron reduction on hexagon carbon sites. The calculations thus further support our hypothesis that with more pentagon/heptagon defect sites, HCNRs exhibit superior ORR catalytic performance than SCNRs.

CONCLUSIONS

HCNRs were fabricated successfully for the first time by pyrolysis of helical MOF nanorods precursors. HCNRs show superior ORR performance *versus* SCNRs, and are even the best amongst dopant-free MOF-derived nanocarbon catalysts. Material characterization and electrochemical measurements attest to the role of topological defects (pentagons/heptagons) in boosting HCNRs with superior activity and a four-electron reduction pathway for ORR. This study clarifies the relative difference between HCNRs and SCNRs in ORR, as well as the significance of spiral effect in ORR promotion. We have thus provided a new perspective for the controllable synthesis of HCNRs and facile design of excellent electrochemical catalysts.

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Author contributions Shi PC, Huang YB, Zhang T and Cao R conceived the project and wrote the manuscript. Shi PC, Liu TT and Yao MS performed the experiments and collected the data. Shi PC, Huang YB and Zhang T analyzed the data. Si DH performed DFT calculations and analyzed the results. All authors discussed the results and commented on the manuscript.

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Supplementary information Supporting data are available in the online version of the paper.

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螺旋碳纳米棒促进电化学氧还原反应性能研究

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摘要 目前螺旋碳纳米材料作为催化电化学反应的催化剂的研究较少。螺旋碳纳米结构对电催化性能的影响更是不明确。本文首次报导以螺旋状的金属有机框架化合物为模板高温热解制备螺旋碳纳米棒。该螺旋碳纳米棒在电催化氧还原反应中展现出比普通碳纳米棒高的催化性能。本文提出了一个制备螺旋碳纳米棒的简易有效的方法, 并为利用螺旋效应设计高效电催化剂提供了新思路。