Preparation of Spiral Nitrogen-Doped Macroscopic Graphene Tube and Tuning the Activity of Oxygen Catalysis by Twisted Ferrum (Fe) Wires

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Abstract: A FeNx-C-based catalyst is considered one of the most promising candidates for the highest oxygen reduction reaction (ORR) activities among nonprecious metal-based electrocatalysts. In this work, a unique catalyst of nitrogen-doped twisted macroscopic graphene tubes decorated with Fe-Nx and bamboo-like carbon nanotubes (CNT) was prepared by using twisted iron wire as a template and cyanamide as a carbon source. The microstructure and physicochemical natures of the samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopic (XPS), X-ray diffraction (XRD), and nitrogen adsorption/desorption measurements. Torsion can promote the dislocation of the iron wire lattice, and activate the surface Fe atoms, thus leading to the growth of bamboo-like carbon nanotubes and forming iron nitride. The product has a graphene-like macroscopic tube structure and exhibits excellent ORR activity. Such excellent ORR performance may be ascribed to the synergistic effect, including high ORR catalytic sites caused by the dislocation of the iron wire lattice, nitrogen heteroatoms doping, favorable reactant transport channels provided by macroscopic tube structure, and fast electron transfer rate induced by 3D continuous networks.

Keywords: twisted iron wires; catalyst; graphene tube; electrocatalytic activity

1. Introduction

Increasing concerns about environmental pollution and energy shortage have initiated a great interest in studying sustainable and clean energy [1]. Electrocatalysts toward oxygen reduction oxygen (ORR) are essential to energy conversion devices with intriguing features, such as fuel cells and metal (e.g., Li or Zn)-air batteries [2]. To date, the Pt/C electrocatalyst is considered to be the state-of-the-art one for ORR application. However, the high cost and scarcity of Platinum (Pt) are the main stumbling block impeding its practical large-scale commercialization [3,4]. To solve these bottleneck problems, enormous attention has been devoted to exploring efficient and low-cost electrocatalysts to substitute the expensive Pt, mainly including low-content precious metal-based materials, transition metal materials and heteroatom-doped carbons [5,6]. Among them, carbon-based transition metal-nitrogen-carbon catalysts (M-N-C, M: Fe or Co), have recently been widely recognized as promising catalysts for ORR in both alkaline and acidic electrolytes [7,8]. For instance, carbon-supported iron group electrocatalysts [9], B,N co-doped carbon dots [10] and Co, N co-doped porous carbons [11] as well as similar materials were high-performance electrocatalysts reported in the literature, which could make large-scale commercialization of fuel cells possible with lower cost in the future.

Recently, one-dimension (1D) carbon materials such as carbon nanotubes, carbon nanofibers and graphene fibers/tubes have attracted extensive attention as a result of their
unique structures and wide potential applications in gas storage, biosensors, supercapacitors, fuel cells and metal-air batteries [12,13]. In contrast to nanoparticles, 1D carbon materials have some unique properties associated with their surface chemistry, unique structure and anisotropy [14,15]. Among them, macroscopic graphene tubes with unique internal hollow channels can provide opportunities for research on chemical reactions, and energy storage and conversions [16]. However, limited synthesis approaches have been developed to prepare the macroscopic graphene tube. To the best of our knowledge, the macroscopic graphene tube has been synthesized using the template strategy via chemical vapor deposition (CVD) containing CH$_4$ and H$_2$, and the electrochemical technique containing graphene oxide. For example, Dai et al. reported that graphene tubes were synthesized by the CVD method using Cu wires as the template [17]. Zhu et al. employed the electrochemical technique to deposit and reduce graphene oxides on a Cu wire [18]. After the removal of the Cu wires by chemical etching for these two methods, the tubular structure composed of highly aligned graphene sheets was formed. Like carbon-based catalysts for ORR, structure tuning is a key strategy to adequately expose the active sites. 1D and 2D carbon materials have different advantages in the active sites and surface chemistry, which influence the electron transfer and mass transport during the ORR process [19].

The catalytic performance is often influenced by both stress and electronic effect. How to tune the stress of the template? It is impossible to separate the effect of force and electronic effect accurately in the experimental process. Torsion can promote the dislocation of metal lattice, activate the surface metal atoms, promote the growth of carbon structures and generate M-Nx active sites [20,21]. However, to the best of our knowledge, there are few reports for the fabrication of Fe-N-C catalysts with bamboo-like carbon nanotubes and spiral hollow graphene tubes for ORR by twisted wire. Thus, the rational design of a novel structure including 1D and 2D carbon materials, with a suitable hierarchical porous structure containing micro-, meso-, and macropores, a high degree of exposure of active sites, and excellent mass and electron transfer ability is highly desirable for achieving outstanding ORR performance.

Herein, we used cyanamide as the solid carbon and nitrogen source, twisted iron (Fe) wires as the growth substrate for growing nitrogen-doped spiral hollow graphene tubes/bamboo-like carbon nanotubes. We found that twisted Fe wires can act as the template and catalyst simultaneously for growing nitrogen-doped hollow graphene tubes and bamboo-like carbon nanotubes. We found that torsion can promote the dislocation of Fe wire lattice, activate the surface Fe atoms, promote the growth of bamboo-like carbon nanotubes and generate iron nitride [20–22]. We now developed a facile method to directly assemble the resultant hollow graphene tubes into macroscopic graphene fibers 100 cm long without much structural damage. The length of the macroscopic graphene fiber thus is determined mainly by the length of the twisted Fe wire used, which is unlimited in principle. The prepared carbon sample is made up of bamboo-like carbon nanotubes/macroscopic graphene tubes and a single Fe composite. The microstructure and physicochemical nature of the samples were characterized by SEM, TEM, XRD, XPS and nitrogen adsorption/desorption measurements, the electrochemical performance was tested by cyclic voltammetry (CV), linear sweep voltammetry (LSV) and cycling stability (I-T), etc. This catalyst here can be synthesized by a simple and scalable method using twisted Fe wires, not only to enhance ORR activity but also to catalyze the bamboo-like CNT growth. This composite catalyst shows a higher ORR activity in alkaline media compared with most nanostructured carbon-based catalysts.

2. Experimental Section
2.1. Chemicals and Materials

Cyanamide was purchased from Aladdin. Nafion solution (5.0 wt%) and commercial 20 wt% Pt/C electrocatalyst were obtained from DuPont and Sigma, respectively. Fe wire and other conventional reagents such as FeCl$_3$, absolute ethanol and HCl were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemical reagents
in this work were analytical grade and directly used without further purification unless pointed out.

2.2. Preparation of Catalysts

The catalysts were obtained by a combination of chemical vapor deposition (CVD) and chemical etching process (Figure 1). In a typical run, twisted Fe wires with a length of 100 cm and a diameter of 0.50 mm were washed with a 1.5 mol/L HCl solution, deionized water and absolute ethanol, and then quickly dried by an electric hair dryer. Then the dried Fe wire was turned round along a graphite rod and the rod was removed, followed by placing the wire in a porcelain boat containing 10 g of cyanamide powder. Subsequently, the porcelain boat with precursors was put in a tubular furnace, and heated at controlled temperatures (800–1000 °C) for 1 h with a rate of 10 °C/min in Ar atmosphere, and then naturally cooled down to room temperature. This resulting black intermediate was rinsed with 2.0 mol/L FeCl$_3$ at 40 °C and repeatedly washed with deionized water until the pH level reached 7. Finally, the black tube samples with a threaded structure were dried in a vacuum oven at 40 °C overnight and denoted as Fe-N$_x$-GNT-y, y represents the relative carbonized temperature.

![Figure 1. (a,b) SEM images of Macroscopic Fe-N$_x$-GNT-2-1000. (c) HRTEM image of Fe-N$_x$-GNT-2-1000. (d) SEM image of Fe-N$_x$-GNT-1000. (e,f) SEM images of Fe-N$_x$-GNT-2-1000. (g) Elemental mappings of Fe-N$_x$-GNT-2-1000 showing the uniform distribution of C, O, N and Fe elements in the green frame area.](image-url)
2.3. Characterization

Scanning electron microscopy (SEM, JEOL, Tokyo, Japan) and elemental mapping were conducted on JSM-7001F equipment (JEOL, Tokyo, Japan). Transmission electron microscopy (TEM) and high-resolution transmission electron microscope (HRTEM) were characterized using a JEOL JEM2010 device (Japan). X-ray photoelectron spectroscopic (XPS) analyses are studied by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha+, USA). X-ray diffraction (XRD) patterns were characterized by X-ray diffractometer (XRD, D8 ADVANCE A25, Germany) with Cu Kα radiation (0.1406 nm). The nitrogen adsorption/desorption measurements were measured using a Micromeritics TriStar II 3020 apparatus (Micromeritics, USA) at a liquid nitrogen temperature (77 K). The Brunauer–Emmett–Teller (BET) specific surface area and porosity were obtained using the Brunauer–Emmett–Teller (BET) method. Before conducting each measurement, all samples were evacuated at 200 °C for 12 h until the pressure was less than 5 × 10⁻³ Torr.

2.4. Electrochemical Measurements

For preparing the catalysts, a glassy carbon (GC) electrode was firstly polished with a 0.05 and 0.3 µm alumina slurry (Gamry RDE710 Rotating Electrode, USA) and subsequently rinsed with deionized water. Then, the GC electrode was sonicated in deionized water, rinsed thoroughly with absolute ethanol and dried in air. To prepare the working electrode, the as-prepared catalyst (5 mg) was ultrasonically dispersed in absolute ethanol (1 mL) and 50 µL of Nafion solution (5 wt%). Then, 20 µL of the resulting ink was dropped on the GC electrode (RDE) surface (diameter: 5 mm) to reach a loading of 0.6 mg cm⁻² and then dried at room temperature overnight. For comparison, a commercial Pt/C catalyst (20 wt% Pt) was prepared using the same process [23,24].

All the electrochemical experiments were carried out on an AutoLab PGSTAT302 N (Metrohm Autolab, Utrecht, The Netherlands) workstation using a three-electrode cell system at 25°C. A three-electrode electrochemical cell equipped with a high-purity O₂ or Ar gas system was employed. All the measurements were performed at room temperature (25 °C) controlled by a thermostatic water bath. A platinum foil (1 cm²) and Ag/AgCl electrodes were used as the counter electrode and reference electrode, respectively. The electrochemical measurements (cyclic voltammograms, linear sweep voltammetry and chronoamperometry) were conducted in 0.1 mol/L KOH aqueous solution to assess the ORR activity of the as-prepared catalysts. Koutecky–Levich (K–L) plot was acquired from the current data at various rotating speeds from 400 to 1600 rpm. The transferred electron number (n) per oxygen molecule was calculated by the K-L equation to identify the oxygen reduction mechanism of the electrocatalyst electrode during the ORR process [25].

\[
\frac{1}{J} = \frac{1}{J_k} + \frac{1}{B \omega^{0.5}}
\]

where \(J_k\) represents the kinetic current density and \(B\) is expressed by the following equation:

\[
B = 0.2nF(D_{O_2})^{2/3}v^{-1/6}C_{O_2}
\]

where \(n\) express the number of electrons transferred per oxygen molecule, \(F\) is the Faraday constant (\(F = 96485 \text{ C mol}^{-1}\)), \(D_{O_2}\) represents the diffusion coefficient of \(O_2\) in 0.1 mol L⁻¹ KOH solution (\(1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}\)), \(v\) shows the kinematic viscosity of the electrolyte solution (\(0.01 \text{ cm}^2 \text{ s}^{-1}\)), \(C_{O_2}\) expresses the concentration of dissolved \(O_2\) (\(1.2 \times 10^{-6} \text{ mol cm}^{-3}\)). The constant 0.2 is adopted when the rotation speed is used in rpm.

3. Results and Discussion

In this work, the cyanamide acted as a solid carbon and nitrogen source and twisted Ferrum (Fe) wires as the growth substrate for CVD growing spiral nitrogen-doped hollow graphene tubes. Interestingly, the twisted Fe wires used in this work can act simultaneously as the template and catalyst for growing spiral nitrogen-doped hollow graphene tubes
and carbon nanotubes. The prepared spiral hollow graphene tubes made into macroscopic graphene fibers were 100 cm long without much structural damage (Figure S1), this length is determined mainly by the length of the twisted Fe wire used. Thereafter, the twisted Fe wire substrate was removed by etching in an aqueous mixture solution of Ferrum chloride (FeCl₃, 1 M) and hydrochloric acid (HCl, 2 M), leading to spiral nitrogen-doped hollow graphene tubes. Finally, the spiral graphene tubes with a porous structure formed (Figure S2). The catalyst labeled as Fe-N-GNT can be synthesized by this simple and scalable method using spiral Fe wires without CH₄ or H₂. This strategy not only can boost ORR activity but also can catalyze bamboo-like CNT growth. Spiral hierarchical macroscopic Fe-Nₓ-GNT was prepared via a transformation of Fe by a feasible direct-synthesis approach in the inert Ar atmosphere and was also free of any physical or chemical activation as shown in Scheme 1. After carbonization, washing and further calcination, the twisted Fe template was removed during the washing treatment. The as-prepared spiral macroscopic graphene tubes decorated bamboo-like carbon nanotubes with Fe and N atoms originating from their starting materials may exhibit outstanding electrochemical activity for ORR [26].

Typical SEM images of the spiral Fe-Nₓ-GNT prepared at 1000 °C; are shown in Figure 1. The Fe-Nₓ-GNT-2-1000 samples possess a spiral macroscopic tube structure with various “stripes” on the surface of the graphene tube due to the Fe wire twisting strain as shown in Figure 1a,b. The macroscopic tubes can be seen in Figure 1c, this spiral morphology may promote the flow of the electrolyte. We can observe the interface between the graphene tube and the Fe wire (Figure 1d) so the formation process of spiral macroscopic tubes is further confirmed. The surface of macroscopic tubes displays a fluffy morphology featuring many large carbon nanotubes and several nanoparticles, showing that an interesting carbon nanotube growing process occurred during heat treatment (Figure S3) [27]. The high-resolution scanning electron microscopy (HRSEM) images illustrate that the as-prepared sample is made up of many fluffy graphene sheets and has a clear microporous structure (Figures 1e, S4 and S5). These images indicate that fluffy graphene sheets can produce a macroporous interpenetrated network, which is typical of heteroatom-doped carbon materials with various FeNₓ particles [28]. These network structures are believed to facilitate the chemistry sorption of reactants at the active sites and eventually enhance catalytic activity. It is suggested that torsion is beneficial for promoting the dislocation of iron wire lattice, activating the surface Fe atoms, boosting the growth of carbon nanotubes and iron nitride and generating more active sites. The elemental mappings reveal a uniform distribution of N and Fe elements on the Fe-Nₓ-GNT-2-1000 (Figure 1g), which shows a well-matched spatial distribution of the two elements, and indicates the successful incorporation of N and Fe atoms into the carbon networks [29].

![Scheme 1](image-url)

**Scheme 1.** Schematic illustration of the procedure for the spiral macroscopic N-doped graphene tube decorated carbon nanotubes and N-Fe particles from a solid carbon and nitrogen source.
The energy-dispersive X-ray (EDX) spectrum (Figure S6) further verifies the presence of dominant peaks for C, O, N and Fe elements in our sample [30]. Additionally, the TEM image (Figure 2) disclosed the presence of large graphene sheets and bamboo-like carbon nanotubes, which were possibly generated by the twisted Fe wire at the high-temperature calcination. The high-resolution TEM image (Figures 2a,b and S1) displays crystallized graphitic layers and ribbon-like graphitic texture, resulting from the lattice dislocation of Fe wire catalyzing the growth of CNTs via active straining. Fe nanoparticles are encapsulated in graphene nanotubes either at the tip or inside of CNTs (Figures S7 and S8), which corresponded to the (002) plane of graphitic carbon and distributed in the Fe nanoparticles encapsulated in several graphene nanotubes [31]. In some instances, Fe nanoparticles can be encapsulated in the graphene nanotubes that are not part of the nanotubes (Figure 2b), which suggests that the encapsulation of Fe into graphene nanoshells may be the first step of the CNT growth. Graphene in the nanotubes was also observed, representing a typical morphological feature of N-doped CNTs synthesized in this work (Figure 2b). A large number of “stripes” are apparent on the carbon nanotubes, and some FeNₓ nanoparticles are sparsely dispersed in the bamboo-like carbon nanotubes and in the graphene tube resembled by its sheet. This graphene structure has an interlayer d-spacing of around 0.34 nm [32] (Figure 2c,d).

![Figure 2. (a,b) TEM images of the Fe-Nₓ-GNT-2-1000 composite catalyst. (c,d) HRTEM images of the as-obtained Fe encapsulated in graphene layer.](image-url)

To further investigate the detailed textural characteristics of the obtained nitrogen-doped twisted macroscopic graphene tubes, nitrogen adsorption-desorption isotherms, XPS and XRD were performed. N₂ adsorption–desorption isotherms of Fe-Nₓ-GNT-2-1000 are shown in Figure 3a. Dramatically, Fe-Nₓ-GNT-2-1000 exhibits a type-IV curve with a pronounced hysteresis loop, suggesting the formation of a mesoporous structure due to residual channel after pyrolysis and removal of the twisted Fe wire template [33]. The
hierarchical twisted macroscopic graphene tubes consist of graphene, carbon nanotubes and single Fe nanoparticles. The specific surface area of the Fe-Nx-GNT-2-1000 sample calculated from the XPS data is 326.2 m² g⁻¹. The mesopore size distribution is in the range of 3–5 nm, which is very important for the migration of electrolyte ions into layers of the catalysts [34].

X-ray diffraction (XRD) was conducted to further analyze the crystal structures of the as-prepared samples (Figure 3b). The XRD patterns reveal that the effect of the twisted Fe wires can obviously affect the phase formation of Fe₂O₃ and Fe₃O₄, which can be identified in the samples. The Fe-Nₓ-GNT-2-1000, after the second calcination, is detected to be lower peak intensity of Fe₂O₃ and Fe₃O₄, whereas only trace elements are detected in Fe-Nₓ-GNT-2-1000 after washing with acid/FeCl₃ and second calcination, indicating that some of the inactive species and exposed nanoparticles have been removed except the FeNx nanoparticle wrapped by bamboo-like carbon nanotubes and graphene [35]. Two pronounced XRD peaks at 26.0° and 44.1° appeared after the second calcination at 1000 °C, corresponding to (002) and (001) planes of graphite, respectively [36]. The peak at about 26° is assigned to the (002) plane of carbon in Fe-Nₓ-GNT-2-1000, but this peak becomes sharper after the second calcination, indicating the increase of the graphitization degree [37]. Especially for Fe-Nₓ-GNT-2-1000, a typical strong peak is observed at about 50°, in agreement with the morphology feature of bamboo-like carbon nanotubes. After acid/FeCl₃ leaching and the second calcination, the patterns of the respective carbon peaks show pronounced change. It has been reported that a Fe compound as a graphitization catalyst can lead to graphitization by a complex process involving the dissolution of carbon atoms into the catalyst, followed by the precipitation of graphitized carbon and the generation of a highly porous structure [38], which is significant for creating more active sites, high electrical conductivity and thus enhancing ORR activity.

As shown in Figure 4a,b, the Fe-Nₓ-GNT-1000 and Fe-Nₓ-GNT-2-1000 samples reveal predominant peaks centered at 283.5, 531.4, 399.4 and 700.1 eV, corresponding to C 1s, O 1s, N 1s and Fe 2p, which confirm the presence of C, O, N and Fe elements [39]. A weak peak at 700.1 eV is attributed to Fe₂p in the spectrum of Fe-Nₓ-GNT-2-1000, revealing that most of the Fe atoms generated from twisted Fe wire are successfully removed. Meanwhile, this confirms that N and Fe atoms have been successfully incorporated into the macroscopic graphene tubes [40]. The contents of N and Fe elements of the Fe-Nₓ-GNT-2-1000 were calculated to be 1.84 at% and 0.51 at%, respectively. The high-resolution C 1s spectrum (Figure 4d) of Fe-Nₓ-GNT-2-1000 can be fitted into several components, attributable to C–C, C–C, C–N, and C=O [41]. In the high-resolution N 1s spectrum of Fe-Nₓ-GNT-2-1000 (Figure 4f), mainly three types of N-functional groups, pyridinic-N (398.2 eV), pyrrolic-N (399.9 eV) and graphitic-N (401.3 eV) can be resolved, which are typically observed in the
case of N-doped carbons and N-Fe [42]. These results further indicate that the as-obtained Fe-N$_x$-GNT-2-1000 have been successfully functionalized by the N and Fe atoms, which have been designed to functionalize various species into the carbon frameworks toward high-performance materials [43]. XPS N 1s spectra can be deconvoluted into three typical peaks. The spiral hierarchical porous structure consists of disordered carbon with a uniform framework. These results further prove the developed porous structure, which is consistent with the TEM and SEM results and expected to facilitate the diffusion of reactants in the electrochemical process [44].

Figure 4. (a) Survey scan XPS spectrum of Fe-N$_x$-GNT-1000. (b) Survey scan XPS spectrum of Fe-N$_x$-GNT-2-1000. (c) C1s spectrum of Fe-N$_x$-GNT-1000. (d) C1s spectrum of Fe-N$_x$-GNT-2-1000. (e) N1s spectrum of Fe-N$_x$-GNT-1000. (f) N1s spectrum of Fe-N$_x$-GNT-2-1000.

To gain insight into the ORR activity of the as-prepared Fe-Nx-GNT, we first carried out cyclic voltammetry (CV) measurements to screen the electrocatalytic activity of activities of the Fe-N$_x$-GNT-2-1000 and the referenced Pt/C catalysts in Ar and O$_2$-saturated
0.1 M KOH solution using cyclic voltammetry at a scan rate of 10 mV s$^{-1}$. As shown in Figure 5a, in the Ar-saturated solution, only the featureless capacitive curve can be gained for Fe-N$_x$-GNT-2-1000. When it was subjected to the O$_2$-saturated 0.1 M KOH solution, a well-defined cathodic peak centered at 0.78 V is observed obviously, signifying its superior electrocatalytic activity toward ORR. Moreover, Fe-N$_x$-GNT-2-1000 shows the most positive oxygen reduction peak among the four catalysts here, confirming that Fe-N$_x$-GNT-2-1000 has the most optimized ORR catalytic activity (Figure S9). To further investigate the ORR activity of the Fe-N$_x$-GNT, steady-state linear sweep voltammetry (LSV) curves have been exerted as shown in Figure 5b. The limiting current densities ($J$) were found to be 2.45, 3.53, 5.06 and 4.46 mA cm$^{-2}$ for Fe-N$_x$-GNT-800, Fe-N$_x$-GNT-900, Fe-N$_x$-GNT-1000, Fe-N$_x$-GNT-2-1000 and Pt(20 wt%)/C, respectively. Especially, the half-wave potential ($E_{1/2}$) of the Fe-N$_x$-GNT-2-1000 was found to be 0.802 V, which is superior to the other samples and approaching commercial Pt(20 wt%)/C, respectively. Notably, Fe-N$_x$-GNT-2-1000 exhibited the best ORR performance among all Fe-N$_x$-GNT samples (Figure S10), with a similar half-potential, superior onset potential (0.845 V) and better limiting current density (5.06 mA cm$^{-2}$) compared to the Pt/C catalyst in completely same measure conditions. This indicates that more active sites were generated by torsion, which promote the dislocation of iron wire lattice, activate the surface Fe atoms, promote the growth of carbon nanotubes and generate iron nitride. The slope of Tafel is an important indicator for evaluating the ORR kinetics. Figure S11 is the Tafel slope obtained by the linear fitting of the corresponding LSV curve according to the Tafel equation ($h = \log j + a$). Among the prepared samples, Fe-N$_x$-GNT-2-1000 had the lowest Tafel slope (58.93 mv dec$^{-1}$), indicating enhanced catalytic kinetic processes.

One of the major concerns for fuel cells in application and commercialization is the utilization and durability of catalysts [41]. To evaluate the accelerated durability, the Fe-N$_x$-GNT-2-1000 has been carried out by continuous CV cycling within a potential range from 1.0 to 0 V (vs. Reversible Hydrogen Electrode (RHE)). After continuous CV cycling, the LSV curves of the Fe-N$_x$-GNT-2-1000 catalyst in O$_2$-saturated 0.1 M KOH solution before and after 2000 cycles were further tested (Figure 5d). Interestingly, after testing for 2000 cycles, the LSV curves in alkaline electrolyte exhibit almost identical onset potential and half-wave potential as the initial ones, suggesting superior long-term stability of our Fe-N$_x$-GNT-2-1000 sample than that of Pt/C under the same test conditions (Figure S12) [49]. The higher durability of Fe-N$_x$-GNT-2-1000 compared with the commercial Pt/C catalyst may be resulting from the main factors, such as the higher strength of the twisted Fe wires, and the lack of activity degradation originating from Fe nanoparticle dissolution and agglomeration due to the wrapped of the nanoparticle by the carbon matrix [50]. The Koutecky–Levich (K-L) analysis was performed to further investigate the ORR kinetics by rotating disk electrode (RDE) measurement at various rotating speeds. K-L plots ($J^{-1}$ vs. $\omega^{-0.5}$) were derived from the LSV curves, and all plots for Fe-N$_x$-GNT-2-1000 showed good linearity (Figure 5e). The electron transfer numbers (n) of the Fe-N$_x$-GNT-2-1000 determined from the slopes of K-L plots, were 3.9–4.0, consistent with a four-electron transfer process for ORR. Evidence to support this hypothesis is found in the kinetic current densities determined from the intercepts of K-L plots, proof for smoother reactant diffusion to active sites on account of that sample’s high BET and highly porous structure. Additionally, the Fe-N$_x$-GNT-2-1000 also displayed a better methanol tolerance level than the referenced Pt/C electrocatalyst as shown in Figure 5f. The chemical composition with Fe-N$_x$ of the Fe-N$_x$-GNT-2-1000 is responsible for this improved accelerated durability and resistance to poisoning.
a). Among the prepared samples, Fe-N\textsubscript{x}-GNT-2-1000 had the lowest Tafel slope (58.93 mV dec\textsuperscript{-1}), indicating enhanced catalytic kinetic processes.

Figure 5. (a) CV curves of Fe-N\textsubscript{x}-GNT-2-1000 in Ar, O\textsubscript{2}-saturated 0.1 M KOH solution at a scan rate of 10 mV s\textsuperscript{-1}. (b) LSV curves of Fe-N\textsubscript{x}-GNT-800, Fe-N\textsubscript{x}-GNT-900, Fe-N\textsubscript{x}-GNT-1000, Fe-N\textsubscript{x}-GNT-2-1000 and Pt/C 20% in O\textsubscript{2}-saturated 0.1 M KOH solution at a scanning rate of 10 mV s\textsuperscript{-1} with 1600 rpm. (c) LSV curves for Fe-N\textsubscript{x}-GNT-2-1000 in O\textsubscript{2}-saturated 0.1 M KOH solution at a scanning rate of 10 mV s\textsuperscript{-1} at different rotation speeds. (d) LSV curves of Fe-N\textsubscript{x}-GNT-2-1000 before and after cycling for 2000 cycles with a rotation rate of 1600 rpm. (e) K–L plots for the ORR in O\textsubscript{2}-saturated 0.1 M KOH solution for Fe-N\textsubscript{x}-GNT-2-1000. (f) The durability test of Fe-N\textsubscript{x}-GNT-2-1000 and Pt/C for methanol. The catalyst loading is 0.6 mg cm\textsuperscript{-2} in all cases.

The spiral macroscopic graphene tube and bamboo-like carbon nanotube structure, specific surface area and hierarchical porous structures of the Fe-N\textsubscript{x}-GNT-2-1000 affect the electrocatalytic performance. Nitrogen doping can create abundant active sites for oxygen reduction reaction, while specific surface area and pore structure efficiently improve the gas diffusion on the Fe-N\textsubscript{x}-GNT-2-1000 surface and the mass transport [51]. The Fe-N\textsubscript{x}-GNT-2-1000 possessed the N heteroatoms, Fe atoms and the largest specific surface area, and thus displayed the best electrocatalytic property according to the onset potential, half-wave potential, limiting current density and electron transfer number. Given
the outstanding electrocatalytic performance, abundant resources, facile preparation and regeneration stability, we find that torsion can promote the dislocation of iron wire lattice, activate the surface Fe atoms, promote the growth of bamboo-like carbon nanotubes and generate iron nitride. G. Yasin et al. [52] reported that the stability and activity of an electrocatalyst are influenced by the internal strain effects from designing the microstrain or localized lattice strain that impacts its surface electronic structure and binding energy toward an adsorbate for oxygen. Thus, this twist strategy can provide a new judicious engineered method of improved electrocatalyst for ORR.

4. Conclusions

In summary, we have demonstrated a facile and simple strategy that was reported for the first time based on stress-twisted Fe wires for preparing the ORR catalyst with the novel structure of a spiral nitrogen-doped macroscopic graphene tube. The microstructure and physicochemical properties of the samples were characterized by SEM, TEM, XPS, XRD and nitrogen adsorption/desorption measurements and the electrochemical performances were tested by CV, LSV and I-T. Torsion can promote the dislocation of the iron wire lattice, activate the surface Fe atoms, promote the growth of bamboo-like carbon nanotubes and generate iron nitride. Thus, the spiral Fe-Nx-GNT-2-1000 hollow tubes decorated with bamboo-like carbon nanotubes and iron-nitride nanoparticles show superior ORR activity comparable to that of commercially available Pt/C in alkaline media, with good half-wave potential approaching benchmark Pt/C and electron transfer number close to 4. The synthetic strategy described in this work is facile and expected to underpin future research efforts to develop nonprecious metal electrocatalysts for ORR and other energy conversion techniques.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/met12122050/s1.

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