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# An efficient bifunctional electrocatalyst from natural cotton fibers for ORR/OER and electric field polarization effect

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# Abstract

Developing efficient bifunctional electrocatalysts that drive both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is significant for renewable energy conversion and storage technologies. In this paper, we report a new method for synthesizing carbon nanostructures through catalytic thermolysis of natural cotton fibers. Pre-treated cotton with Fe annealed under ammonia gas environment at an optimized temperatures 900°C yielded nitrogen-iron doped carbon (NFe/C) with bamboo-like structures. Our experimental measurements show that NFe/C synthesized at 900°C (NFe/C (900°C)) possess good bifunctional electrocatalytic activities toward ORR and OER, with an excellent stability in alkaline electrolytes. We further studied the electric field polarization effect on NFe/C (900°C) by utilizing a DC electric field on the catalyst ink drop casted on a glassy carbon electrode. Interestingly, the applied electric field created a dielectrophoresis phenomenon that assisted the packing of the catalyst particles, and resulted in a compact catalyst

electrode with an improvement of electrocatalytic performance, that have not been previously explored. The reported new synthesis method using natural cotton and the electric field polarization effect have the potential to achieve a low cost and mass production capability for producing carbon-based noble-metal-free bifunctional electrocatalysts for green energy conversions.

**Keywords:** natural cotton fibers; Oxygen Reduction Reaction; oxygen evolution reaction; electric field; renewable energy conversion; storage technologies

#### 1. Introduction

Global energy challenges lead to the research of renewable electrochemical energy conversions to be of paramount importance for future environmental and energy applications [1]. Regenerative fuel cell (RFC) working as an energy conversion system can fulfil this requirement. It consists of two key electrochemical processes, oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), which are integrated into one unit rendering a unitized regenerative fuel cell (URFC) [2, 3]. Considering the myriad advantages of URFC over conventional secondary batteries, such as high specific energy density (above 400 Wh kg<sup>-1</sup>), long-term energy storage property and no self-discharge [4, 5], they can be used in space applications serving space vehicles or stations by cooperating with the solar array and also in terrestrial applications [6, 7].

Development of bifunctional oxygen catalysts (BOCs) driving both ORR and OER is the main element in URFC technology. Owing to the sluggish kinetics in the electrocatalytic reduction and evolution of molecular oxygen [8], the promising BOCs are limited to several noble metals and their oxides, i.e., Pt, Ir, Ru, IrO<sub>2</sub> and RuO<sub>2</sub> [9, 10]. It is appealing for researchers to pursue new, more Earth abundant materials to replace noble metals [11] The materials with high activities, but low cost and environmental friendly, are highly demanded [12]. Therefore, developing inexpensive BOCs retaining high catalytic activity, long-term durability, and reasonable electronic conductivity is challenging.

The high electrical and thermal conductivities, high mechanical strength and chemical stability of carbon nanotubes (CNTs) make them very useful for electrochemical

technologies. A broad applicability can be fulfilled upon decreasing the cost of CNT production. In this paper, we report the results of our recent explorations for a new method to synthesize carbon micro & nano structures, some with tubular structure, based on a catalytic thermolysis of natural raw cotton fibers, which are renewable and sustainable agricultural products. The reported method can be used to transform the textile bio-waste to carbon nano materials, which represents a significant advantage in terms of both economic gain and solid waste recycling. Nitrogen-doped carbon nanotubes (N-CNTs) like noble-metal-free electrocatalysts have attracted a great attention as efficient ORR [13-15] and OER electrocatalysts [16, 17]. Investigations of bifunctional catalysts have shown that noble-metal-free nitrogen-doped carbon based nanomaterials can serve as a good BOC [18-20].

In this work, we synthesized nitrogen-iron doped carbon (NFe/C) prepared from natural cotton fibers at different temperature range from 800°C to 1100°C; afterwards, we named them as NFe/C (temperature °C). NFe/C (900°C) shows superior oxygen electrode activities (OEA) compared to noble metal catalysts with an excellent stability in alkaline solution. Furthermore, we studied the electric field polarization effect of NFe/C samples on their electrocatalytic properties, which has not been explored so far for such materials. Applying an electric field cause Columbic attraction between carbon nano objects due to the polarization of nano materials [21]. In this work, we found that applying electric field on the samples could produce a closely packed electrocatalyst electrode with an improvement in the conductivity. The developed new method of obtaining NFe/C catalysts with good bifunctional electrocatalytic properties may open new opportunities for new fuel cell applications by using earth-abundant, scalable, and carbon-based materials as cost effective and high performance catalysts. Applying an electric field to polarize carbon based materials can also pave an interesting way to improve their electrocatalytic properties.

#### 2. Experimental

# 2.1 Synthesis of materials: (NFe/C (800°C), NFe/C (850°C), NFe/C (900°C), NFe/C (950°C), NFe/C (1000°C), and NFe/C (1100°C)

Firstly, natural cotton fibers were pre-treated in a diluted acid solution (0.5M HNO<sub>3</sub> or 0.5M  $H_2SO_4$ ) at 60°C - 70°C for 6 hours to remove dirt and other impurities. The pre-treated cotton

(1g) was then soaked in a well dissolved solution of iron acetate (1 g) and cyanamide (3.5g) in 500 mL ethanol, stirred at 75 °C until the ethanol was evaporated, followed by a heat treatment in vacuum oven at 70 °C until the cotton was completely dried. By a heat treatment for 1 h in ammonia environment at different temperatures (800 °C, 850 °C, 900 °C, 950 °C, 1000 °C, and 1100 °C), the treated cotton can be converted to Fe/nitrogen/carbon tubs like/carbon nanoparticles (Fe/N/CT/CNP) composite through a catalytic thermolysis. To remove the redundant metallic iron and iron compounds which attached physically to the surface of the sample, the obtained Fe/N/CT/CNP composite were purified in 0.5 M HNO<sub>3</sub> or 0.5M H<sub>2</sub>SO<sub>4</sub> at 70 °C overnight. Finally, the sample was heat-treated again under the same conditions as used for the first heat treatment.

**Labelling the samples:** The sample prepared at temperature of 900°C named as NFe/C (900°C) afterwards, indicating iron-nitrogen doped carbon material heat-treated at this temperature. Similarly, the sample synthesized at temperature of 950°C tagged as NFe/C (950°C) afterwards. Also, the sample obtained at temperature of 1000°C labelled as NFe/C (1000°C), and finally if the temperature used for heat treatment was 1100°C, the sample named as NFe/C (1100°C). The value in the bracket represents the heat treatment temperature and "NFe/C" indicates N and Fe doped carbon.

#### 2.2 Synthesis of un-doped carbon sample from cotton [22]

In addition, we compared the electrocatalytic properties of the above samples with the carbon material from cotton without N-doping. The synthesis procedure of this material has been reported in our previous publication [22]. For this experiment, the pre-treatment procedure of the cotton fibers is the same as discussed in the above section. Instead of using ammonia gas, the pre-treated cotton fibers were treated at 1200°C for 1 h in hydrogen environment for a hydrogen reduction. This procedure was used to convert the cotton fibers to carbon material without N-doping.

#### **2.3 Electrochemical Measurements**

All measurements were carried out at room temperature using a potentiostat (A-METEC) with a three-electrode electrochemical cell. Rotating disk electrode (RDE) and Ring disk electrode (RRDE) measurements were performed on Pine instrument. We used an interchangeable glassy carbon (GC) disk electrode with a 5-mm diameter (area 0.196 cm<sup>2</sup>) as the working electrode, a platinum (Pt) wire as the counter electrode, and Hg/HgO (in saturated KOH solution) as the reference electrode. The potential of

the reference electrode (Hg/HgO) in 0.1 M KOH shifts to 0.95 V RHE (supporting information, Figure S1). The GC disk was mechanically polished to achieve a mirrorlike finish on the top surface of the electrode. Finally, the GC electrode was sonicated in ultrapure water, ethanol, and then again in ultrapure water and dried at room temperature before applying the catalyst ink. Linear sweep voltammetry (LSV) measurements were performed in O<sub>2</sub>-saturated 0.1 M KOH solutions at scan rate of 10 mVs<sup>-1</sup>. RDE measurements were performed at rotation rates varying from 500 to 2500 rpm depending on the measurement, with the scan rate of 10 mV s<sup>-1</sup>.

To prepare the catalyst ink for electrochemical measurements, 5 milligrams of the synthesized sample was mixed with the following solution: 1.25 mL of 3:2 Isopropanol/water solution, and 50  $\mu$ l Nafion (5 wt %). This solution was sonicated for 1 h to achieve homogenous ink. Then a 20  $\mu$ l drop of the catalyst ink was loaded on the polished surface of the glassy carbon electrode (GCE) and dried slowly at room temperature to achieve a uniform surface. Once the sample was completely dried, we estimated the amount of the sample delivered to the surface was 400  $\mu$ g/cm<sup>2</sup>. The sample was used in electrochemical measurements immediately after drying. Finally, Pt/C catalyst was used for comparisons and prepared exactly as the synthesized sample to achieve a similar loading of 400  $\mu$ g/cm<sup>2</sup> of Pt/C (20 wt. %).



**Figure1.** Schematic illustration for the preparation of NFe/C material through a catalytic thermolysis of natural cotton fibers followed by applying DC electric field polarization on the prepared catalyst.

The GC electrode with catalyst ink was inserted between two electric electrodes and a DC electric filed was applied till the catalyst ink completely dry. Figure 1 shows the schematic procedure for the sample preparations and the experimental apparatus used for DC electric field polarization to the electrocatalyst ink. The electric field was applied by using two parallel electrodes with DC voltage supplied between 0 to 150 V using a DC voltage apparatus (HSPY-400-01, Hanshengpuyuan Company). The gap between the DC electrode and the surface of ink sample on GCE was 1.5 mm. After the catalyst ink dried under the electric field, the interchangeable working electrode was then inserted into the electrode shaft of RDE measurement instrument, followed by measuring the electrochemical properties of electrocatalysts. For the sample exposed to the electric field using for example 150 V, the electric field was 100 V/mm. So we name the sample as NFe/C(900°C) [100 V/mm] afterwards, here the value in the bracket refers to the applied electric field strength.

#### **2.4 Characterizations**

The morphologies of the obtained samples were firstly characterized by using scanning electron microscopy (SEM) (JSM 6610LV, JEOL, Japan) operating at 15 KV. The microstructure of the samples was characterized by using transmission electron microscopy (TEM) at 120 KV (JEM-1400, JEOL, Japan). For TEM studies, a drop of sonicated material suspension in ethanol was placed on a copper grid, followed by drying under ambient condition. The high resolution TEM (HRTEM) images of material samples were completed by using JEM–2100F operating at the acceleration voltage of 200KV (JEOL, Japan). Kratos Axis 165 x-ray photoelectron spectroscope (XPS) was used to measure XPS spectra of the samples using Al K $\alpha$  1486.6 eV x-rays. High resolution spectra of C-1s, N-1s, O-1s and Fe-2p were collected on the samples. During data acquisition runs, passing energy of 160 eV, current at 10 mA, and a time of 20 ms per step were used.

#### 3. Results and Discussions

The structure of our sample was studied by X-ray diffraction (XRD) using a MiniFlex 600 benchtop machine (Regaku, Japan) with 2 $\theta$  scanning range from 10° to 80°. The XRD pattern of the produced un-doped carbon material (prepared under hydrogen atmosphere) is presented in Figure 2(a). The sharp narrow diffraction peak at 2 $\theta$  = 26.38° is the characteristic diffraction signal from graphitic interlayers (0 0 2) with an interlayer distance of 3.38 Å. This peak reflects the graphitic character of the CNTs [23], which is comparable to the distance between graphene layers in graphite. The relatively weak peaks around 43° show the characteristic turbostratic graphite (1 0 0) layers in MWCNTs [24]. The peak positioned at 2 $\theta$  = 48° is related to (101) [25].

Figure 2(b) shows XRD the patterns of NFe/C (900°C). Diffraction peaks assigned to multiwalled carbon nanotubes (MWNTs) at  $2\theta = 27^{\circ}$  and  $43^{\circ}$  and  $48^{\circ}$  can be clearly seen in the XRD curves, indicating that the MWNT structure was not destroyed after doping. The XRD patterns in Figure 2(b) (blue curve) show typical characteristic peaks [(311), (222), (400), (110), (422), (511)] of Fe<sub>3</sub>O<sub>4</sub> which are in agreement with the standard values (JCPDS card no. 75-0033) [26]. Due to the presence of nitrogen functionalities in the NFe/C (900°C), there is a small shift towards higher 2 at (002) peak. This may be due to the incorporation of nitrogen in the structure of nanotubes that creates slight distortion in graphene stacking regularity along *a* or *b* direction and shorter C-N bonds than C-C bond. This phenomenon has been seen before [27], [28].



**Figure 2.** XRD patterns of the produced samples: (a) carbon material without N-doping, (b) NFe/C(900°C). Fe<sub>3</sub>O<sub>4</sub> peaks are distinguished by green stars. Diffraction peaks assigned to multi-walled carbon nanotubes (MWNTs) are marked by underlines.



Figure 3. (a) SEM images of (a) un-doped carbon, (b) NFe/C (800°C), (c) NFe/C (900°C), (d) NFe/C (950°C), (e) NFe/C (1000°C), and (f) NFe/C (1100°C).

In order to study the morphology of the synthesized nitrogen-iron dopedCNTs, SEM was used. It can be seen from Figure 3 that the samples have some segments in micron meters. We can see tube-like shapes in all samples together with small carbon particles. Compared to the morphology of un-doped carbon sample, the segments in N-Fe doped carbon samples become much smaller, with more small carbon particles. By elevating the treatment

temperature, we can see the presence of small particles increased. It is hard to find tube-like shapes for NFe/C (800°C) which is due to insufficient temperature for growing the tube-like samples. Figure 3(c) shows that NFe/C (900°C) contains more small carbon particles compared to the other samples Figure 3.



**Figure 4.** (a) TEM images of (a) NFe/C (800°C), (b) NFe/C (850°C), (c) NFe/C (900°C), (d) NFe/C (950°C), (e) NFe/C (1000°C), and (f) NFe/C (1100°C).

Figure 4 (a) to (e) show the TEM images of the produced materials from natural cotton fibers at different heat treatment temperatures. Carbon nanotubes (CNTs), carbon nanoparticles (CNPs), graphene nanoplatelets (GNPs), and remaining Fe particles are observed. Figure 4 (a) illustrates that NFe/C ( $800^{\circ}$ C) includes less tube-like subjects than other samples. This is due to the lack of enough temperature for appropriate synthesis. All samples demonstrate the vicinity of some Fe nanoparticles attached to the surface of carbon sheets. NFe/C ( $900^{\circ}$ C) in Figure 4(c) exhibits many nanoparticles attached to tube-like subjects, due to nitrogen doping. Increasing the treatment temperature, less nanoparticles were found on the samples (Figure 4(d) –(f)).



**Figure 5.** (a) & (b) TEM images of bulk NFe/C(900°C). (c) HRTEM image of iron nanoparticle encapsulated in carbon nanoshells in NFe/C(900°C). (d) Carbon tube growth around an iron catalyst (NFe/C(900°C)). (e) Typical bamboo-like defect in the structure of NFe/C(900°C). (f) High resulation TEM of the joint section of the bamboo structure in NFe/C(900°C). (g) & (h) TEM images of NFe/C(900°C) focusing on the presence of graphene nanoplatelets (GNPs).

In order to elaborate the growth mechanism of FeN-doped carbon nano-structures, high resolution TEM (HRTEM) was used (as shown in Figure 5), aiming to shed some light on how nitrogen doping can change the microstructure. The overall image of bulk NFe/C (900°C) sample shows the presence of Fe/carbon tubes like/carbon-nanoparticles/graphene nanoplatelets (Fe/CT/CNP/GNPs) composite (Figure 5 (a) and (b)). The HRTEM images reveal that iron nano particles are encapsulated in graphene nanoshells (Figure 5(c)) that

resulted in Fe catalysed growth of carbon tubes like (Figure 5(d)). The Fe nano-particles performing as a catalyst in the growth of CTs can be considered as the first step of CTs growth [29]. However, based on SEM and TEM images, we can see some Fe nanoparticles attached to the surface of graphene sheets without being encapsulated.

The TEM image of Fe-nanoparticles with periodic lattices (white boxes) shown in Figure 5(c) corresponds (110) planes indicating interplanar distance of 0.202 nm [30]. Our XRD data of the same sample (Figure 2(b)) also recorded a feature at  $2\theta$ = 44.8° (the (110) reflection of Fe) [30]. We can see the bamboo-like structures and joints from Figure 5 (e) and (f), as the evidence of the presence nitrogen-doped CT as discussed by other researchers [29, 31, 32]. The HRTEM images indicate that the synthesized bamboo structures in NFe/C (900°C) are multi-walled (Figure 5(f)). The interlayer spacing in 3D-crystalline carbon layers at 0.338 nm revealing (002) planes is in agreement with our XRD pattern of the sharp peak at  $2\theta$ =26.38°, that also matches the results of previous reports [33-35]. From Figure 5 (g) & (h), we can also see that NFe/C (900°C) possesses some carbon graphene nano sheets.

Since more nitrogen atoms create more defects in carbon nanotubes like and more bamboo structures [29, 31], it is interesting to see how synthesis temperature changes the bamboo-like morphology of the samples. Figure 6 indicates that by increasing the temperature the percentage of the existence of bamboo-like shapes is getting lower. Consequently, we checked the nitrogen content in the samples to evaluate if we can expect a decrease of nitrogen doping amount by elevating the synthesis temperature. Therefore, XPS was used to measure the nitrogen contents of our samples to support this hypothesis.



Figure 6. (a) TEM images (a) NFe/C (900°C), (b) NFe/C (950°C), (c) NFe/C (1000°C), and

#### (d) NFe/C (1100°C).

XPS spectra of all samples were shown in supporting information (Figure S2 to Figure S5). C1s binding energy (BE) can been seen in Figure S2, indicating sp<sup>2</sup> C (284.7 eV), sp<sup>3</sup> C (284.9 eV), C-O/C-N (286.2 eV), and  $\pi$  excitation (290.7 eV). We can see O1s BE from the XPS spectra in Figure S2; O1: O-C (531.5 eV), O2: O=C (532.4 eV), O3: O-C=O (534.1 eV) [36]. Figure S2 also shows the XPS spectra of functionalized graphene in N1s BE range. The XPS spectra have been fitted to get detailed chemical bonding information of the elements N and O with carbon. Nitrogen is observed in the sample confirming its incorporation into carbon structure. Generally, there are several nitrogen functional groups in nitrogenfunctionalized carbon structure. These include pyridinic-N (N1, BE = 396.1 eV), pyrrolic-N (N2, BE = 400.2 eV), quaternary nitrogen (N3, BE = 401.9 eV), and N-oxides of pyridinic-N (N4, BE = 403.2 eV) [37-39]. The nitrogen functional groups are usually in the following molecular structures (chemical states)[37-39]: pyridinic-N (labelled as N1) refers to nitrogen atoms at the edge of graphene planes, each of them is bonded to two carbon atoms and donates one  $\pi$ -electron to the aromatic  $\pi$ -system; pyrrolic-N (labelled as N2) refers to nitrogen atoms that are bonded to two carbon atoms and contribute to the p system with two  $\pi$ electrons; quaternary nitrogen (labelled as N3) is also called "graphitic nitrogen" or "substituted nitrogen", in which nitrogen atoms are incorporated into the graphene layer and replace carbon atoms within a graphene plane; N-oxides of pyridinic-N (labelled as N4, pyridinic–(N+ - O)) are bonded to two carbon atoms and one oxygen atom. XPS spectrum also shows the peaks at 712 and 725 eV for the binding energies of Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$ , reflecting iron species existed [40].



Figure 7. XPS surveys of (a) NFe/C (900°C), (b) NFe/C (950°C), (c) NFe/C (1000°C), (d)

NFe/C (1100°C), and (e) NFe/C (800°C). Comparisons of the elemental compositions are also shown in the graph.

Figure 7 shows the comparisons of XPS surveys of the samples prepared at different temperatures. We can see that by elevating the synthesis temperature the nitrogen contents in the samples are decreasing. Our hypothesis is that at high temperature the thermal energy can remove the doped atoms in the carbon structure although ammonia gas provided nitrogen atoms for doping; as a result, the chance of being doped on the surface of the sample is getting low. However, owing to the lack of sufficient temperature for appropriate N-doping, NFe/C(800°C) contains less amount of Nitrogen content. The presence of more N-doping in NFe/C(900°C) indicates more defects in the graphene stacking in the sample. This result together with the observation of more bamboo structures (Figure 6(a)) in NFe/C(900°C) compared with other samples may lead to a conjecture that NFe/C(900°C) may possess better electrocatalytic performance because of more nitrogen content. The formation of more exposed graphene edges and high number of bamboo-like joints suggest a better catalytic performance for nitrogen doped carbon structure due to increasing the formation of O<sub>2</sub> adsorption sites [31, 41]. Motivated by this hypothesis, we investigated the electrochemical activity of this sample more carefully.

#### 3.1 Evaluation of Electrocatalytic Activity for ORR and OER

We compared the performance of NFe/C samples for ORR and OER catalyses in alkaline media (0.1 M KOH) saturated in O<sub>2</sub> using LSV. It is also common to perform the two reactions in the same vessel with the aim of seeking a good catalyst for regenerative fuel cell [42-44]. Comparisons of LSV data for unfunctionalized carbon sample [without nitrogen doping (named as un-doped carbon)] and nitrogen functionalized NFe/C(900°C) sample revealed that the presence of nitrogen can enhance the electrocatalytic performance, i.e., higher current density and more positive onset potential for NFe/C(900°C) than un-doped carbon for ORR and OER (Figure 8(a)). The results indicate that the intercalation of nitrogen in the carbon structure can improve electrocatalytic activities for the two reactions.

Figure 8(b) shows the combined OER-ORR performance of NFe/C samples prepared at different temperatures, i.e., 800°C, 850°C, 900°C, 950°C, 1000°C, and 1100°C, as well as a sample of Pt/C (20%-wt.) for comparisons. For the samples prepared at 800°C and 850°C, we could not get a good result due to lack of sufficient temperature for appropriate N-doping. The more positive onset potential and higher current density of NFe/C(900°C) sample in ORR region (compared to other samples prepared at higher

temperatures) indicate that this temperature is more effective for synthesizing the catalyst towards ORR activity. As we mentioned earlier, higher temperatures than 900°C can cause less N-doing and introduce less activity. Although the performance of this sample is not as good as Pt/C when strictly considering ORR, NFe/C(900°C) sample shows a better performance than other samples prepared at higher temperatures, more close to that of Pt 20wt%/C.



**Figure 8.** ORR and OER activities: (a) LSV comparison among NFe/C(900°C), Undoped carbon [the sample without nitrogen doping] & Pt/C (Pt-20 wt%), (b) LSV comparison of NFe/C samples prepared at different temperatures compared to Pt/C (Pt-20 wt%). The LSV measurements were performed in O<sub>2</sub>-saturated 0.1 M KOH, 1600 rpm, 10 mV cm<sup>-2</sup>.

The Tafel equation describes the electrochemical kinetics relating the rate of an electrochemical reaction to the overpotential.[28] The Tafel slope provides insight into the reaction mechanism. Larger Tafel slope indicates that a larger resistance (or a large loss of potential) is necessary to accelerate a chemical reaction. Pt/C 20 wt% exhibits Tafel slopes of 60 and 120 mV dec<sup>-1</sup> at high and low potentials, respectively. Tafel slopes for NFe/C(900°C) in ORR region as shown in Figure S6 demonstrate similar

results as compared to Pt/C 20 wt%.

In order to understand the number of electrons involved in the reaction, which is an important factor for fuel cell applications, Koutecky–Levich plots were used. The corresponding Koutecky–Levich plots ( $j^{-1}$  vs. (angular rotation speed,  $\omega$ )<sup>-1/2</sup>) at various electrode potentials show good linearity for NFe/C(900°C). Linearity and parallelism of both plots are considered as typical first-order reaction kinetics with respect to the concentration of dissolved O<sub>2</sub> (Figure S7). The kinetic parameters can be analysed based on the Koutecky– Levich equations:

$$\frac{1}{j} = \frac{1}{j_{\rm L}} + \frac{1}{j_{\rm K}} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_{\rm K}}$$
$$B = 0.201 \ nFC_0 \ (D_0)^{2/3} \ v^{-1/6}$$
$$J_{\rm K} = \alpha nFC_0$$

Here, *j* is the measured current density;  $j_{\rm K}$  and  $j_{\rm L}$  are the kinetic and diffusion-limiting current densities, respectively;  $\omega$  is the angular rotation speed of the disk (rpm); n is the overall number of electrons transferred in oxygen reduction; F is the Faraday constant (F = 96485 C mol<sup>-1</sup>);  $C_0$  is the bulk concentration of  $O_2$ ;  $\nu$  is the kinematic viscosity of the electrolyte; and  $\alpha$ is the transfer coefficient. The curve  $j^{-1}$  vs.  $\omega^{-1/2}$  is a straight line characterized by slope  $(nB)^{-1}$ and intercept  $(j_{\kappa}^{-1})$ . The slope of the straight line enables the extraction of the total number of exchanged electrons *n* and the intercept at the origin gives the inverse of the kinetic current  $j_{\rm K}$ by using parameters  $C_0 = 1.2 \times 10^{-3} \text{ molL}^{-1}$ ,  $D_0 = 1.9 \times 10^{-5} \text{ cms}^{-1}$ , and  $v = 0.1 \text{ m}^2\text{s}^{-1}$  in 0.1M KOH. ORR can occur either via a direct 4-electron reduction pathway where O<sub>2</sub> is reduced to H<sub>2</sub>O, a 2-electron reduction pathway where it is reduced to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), or an indirect 4-electron reduction pathway where the generated  $H_2O_2$  is further reduced to  $H_2O$ . The number of electrons transferred at potential 0.45 V for NFe/C(900°C) is 3.67 while 2.70 electrons transferred using NFe/C(1000°C) (Figure S8). The number of electrons evolved in the reaction at 0.45 V for NFe/C(950°C) is 2.45 and toward NFe/C(1100°C) is 2.18. Thus, NFe/C(900°C) sample prepared at 900°C shows better activity towards ORR compared to the other samples, forming about 4 electrons during ORR, which is in agreement with previous papers [45-48]. This indicates that NFe-doped catalysts can enhance the catalysis performance. According to our SEM and TEM images, there are several Fe nanoparticles attached to the surface of graphene sheets without being encapsulated, we expect this Fe content may also enhance the catalytic ORR performance. In addition, our previous results based on firstprinciples spin-polarized density functional theory (DFT) calculations[49] for the electrocatalytic reaction steps on the FeN<sub>4</sub>/C site of carbon nanotubes, showed the same finding. O<sub>2</sub> molecule can be adsorbed and partially reduced on FeN<sub>4</sub>/C site without any activation energy barrier. The partially reduced O<sub>2</sub> further reacts through a direct pathway (DPW) and form water molecules without any activation energy barrier. Through an indirect pathway (IDPW), there is an activation energy barrier of ~0.15 eV for the formation of the H<sub>2</sub>O molecule. The NFe/C(900°C) sample contains short length carbon nanotubes with more opening edges compared to other samples, which agree with our previous conjecture that pyridinic-type sites on the open edges of nitrogen-doped carbon nanotubes may contribute to the high catalytic activity for ORR [50].

Recently Yang et al.[51] showed that the presence of quaternary N (graphitic N, N-bonded to three carbon atoms) atoms which have relatively low energetic barrier for donating electrons from the surface of the catalyst can also be responsible for ORR. The quaternary N atoms in graphene-typed structure could give electrons to the  $\pi$ -conjugated system so that it can increase nucleophile strength of the adjacent carbon rings [C( $\delta^-$ )] and improve O<sub>2</sub> adsorption. Since O<sub>2</sub> has high densities of O lone pair electrons [O( $\delta^+$ )], the presence of [C( $\delta^-$ )] can enhance ORR [52, 53].

The role of the real "electrocatalytically active sites" still remains in debate since their contribution to the catalytic activity is not well defined [54]. In some studies, the enhanced electrocatalytic activity is attributed to pyridinic-N and/or pyrrolic-N [37-39]. Miyata suggested that graphitic nitrogen is more important for the electrocatalytic activity of nitrogen-doped carbon [55]. Our XPS results indicate that N-graphene also exists in all the samples. It is believed that carbon atoms adjacent to nitrogen dopants possess a substantially higher positive charge density to counterbalance the strong electronic affinity of the nitrogen atom [32], which results in an enhanced adsorption of  $O_2$  and reactive intermediates (i.e., superoxide, hydroperoxide) that proceeds to accelerate the ORR [31, 50]. The nitrogeninduced charge delocalization could also change the chemisorption mode of O2 from monoatomic end-on adsorption on undoped carbon to a diatomic side-on adsorption at nitrogen functionalized carbon structure which effectively weakens the O-O bond to facilitate ORR [32]. This is also true for  $H_2O_2$  reduction because breaking the O–O bond is also a key step for the electrocatalytic reduction of H<sub>2</sub>O<sub>2</sub>. In addition, the presence of nitrogen in the structure enhances the ability of graphene sheets to donate electrons [38], which is advantageous for reduction reactions.

The OER region from 1.0 V to 2.0 V can be seen in the upper section of Figure 8. Examining meticulously at OER curve, three different electrochemical processes (1.0 V to 1.4 V, 1.4 V to 1.7 V, and after 1.7 V) can be identified. The tail structure (from 1.2 V to 1.4 V) might be due to carbonaceous species oxidation process before OER starts, as there are several oxygen groups on the sample surface that were confirmed by XPS results.

In the OER region, the ascending curve for NFe/C(900°C) starts earlier than the results of other NFe/C samples as shown in Figure 8. This indicates that NFe/C(900°C) is much more favourable for water oxidation, which requires less overpotential to drive this reaction. The potential at I = 10 mA.cm<sup>-2</sup> for NFe/C(900°C) is about 1.75 V, which is lower than that of other samples. The results show that the performance of active sites on the surface of NFe/C(900°C) is better than other NFe/C samples prepared at different temperatures. NFe/C(900°C) sample is more favourable as a better catalyst for OER as well. Yang et al. showed that the adsorption of OOH\* and O\* intermediates on carbon atoms next to the pyridinic N is responsible for OER [51]. Pyridinic N (an electron-withdrawing group with the lone pair electrons involved in the resonance to delocalize electrons to make the N atoms electron-deficient) can accept electrons from adjacent C atoms  $[C(\delta^+)]$ , facilitating the adsorption of water oxidation intermediates (OH<sup>-</sup>,OOH<sup>-</sup>) from catalyst surface [56, 57]. Owing to the fact that Pt is not a good catalyst for OER, we also compared the performance of our samples with Ir and Ru catalysts, which are well-known precious metal catalysts for OER (Table 1). The OER activities of NFe/C(900°C) sample are comparable to those of precious metal catalysts.

The electroactive surface area of NFe/C(1000°C), NFe/C(1100°C), NFe/C(950° C) and NFe/C(900°C) were examined by studying the redox reactions involving Fe(CN)<sub>6</sub><sup>3-/4-</sup> (**Figure S9**) using cyclic voltammetry (CV). Cyclic voltammetry of two samples performed in 10 mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> / 1 M KCl. The electroactive surface area can be calculated by using the Randles-Sevcik equation [58, 59]:  $i_p = 2.99 \times 10^5 n \text{ A C D}^{1/2} v^{1/2}$ 

where  $i_p$ , n, A, C, D and v are the peak current, the number of electrons involved in the reaction, the electroactive surface area, the concentration of the reactant, the diffusion coefficient of the reactant species, and the scan rate, respectively. The redox reaction of Fe(CN)<sub>6</sub> <sup>3-/4-</sup> involves one-electron transfer (n = 1), and the diffusion coefficient (D) is 6.30 ×10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup>. The electroactive surface area for NFe/C(900 °C) is 0.619 cm<sup>2</sup>, which is higher

than the other samples (Figure S9). These results confirm that NFe/C(900°C) is a better electrocatalyst with higher electroactive surface area enhancing the charge transfer kinetics on the electrode surface. The high electroactive surface of NFe/C(900°C) among the other samples maybe the major impact on ORR-OER catalytic activity.

The durability/stability of the obtained NFe/C(900°C) as ORR -OER catalyst was evaluated against Pt/C electrode. The test was performed using chronoamperometry in 0.1M KOH solution saturated with O<sub>2</sub> (Figure S10). The corresponding current–time chronoamperometric response of NFe/C(900°C) exhibits a very slow attenuation with only 13% decay for ORR region over 8000 s. In comparison Pt/C 20wt% showed 26% decay for ORR region. This demonstrated that the durability/ stability of NFe/C(900°C) catalyst is better than that of Pt catalyst. To confirm the reversibility of the catalysts, LSVs were measured using forward and backward currents as illustrated in Figure S11. Observation of the same LSV futures of running forward and reverse currents reveals that the sample has a good reversibility for both reactions. This result reveals that performing the electrochemical measurement *via* starting from ORR region or OER region has no effect on the catalytic performance. Consequently, this catalyst can be used for regenerative fuel cell.

#### 3.2 Electric Field Polarization Effect on Electrocatalytic Properties

We also studied the electric field polarization effect on the electrocatalytic properties of the catalyst sample. We compared the performance of NFe/C(900 °C) for ORR-OER catalysts in alkaline media (0.1 M KOH) saturated in O<sub>2</sub> using LSV after applying various DC electric fields. Interestingly, after polarizing the catalyst by 100 V/mm DC electric field, the electrocatalytic performance of NFe/C(900 °C) (Figure 9) was improved. Herein, NFe/C(900°C) [100 V/mm] in Figure 9 refers to the sample after applying an electric field 100 V/mm. The overpotential of ORR for the sample was reduced by applying electric field polarization to the sample, approaching to that of Pt catalyst. We did not see a significant difference regarding performance in OER.



**Figure 9.** (a) LSV data of Pt /C 20 wt% and NFe/C(900°C) samples with electric field polarization; the values in the brackets indicate the electric field strength. (b) LSV data of Pt /C 20 wt% and NFe/C(900°C) samples with electric field polarization in ORR region; (c) LSV data of Pt /C 20 wt% and NFe/C(900°C) samples with electric field polarization in OER region.



**Figure 10**. (a) & (c) SEM images of the electrode surface made of N-CNTs(900 °C) without an applied electric field polarization; (b) and (d) SEM images of the electrode surface made of NFe/C(900°C) [100 V/mm].

Applying an electric field higher than 100 V/mm can cause an aggregation of the catalyst powders to the middle of the electrode surface and reduce the total effective electrode surface area (Figure S12). In the presence of an electric filed, each NFe/C particle/tube undergoes a polarization. Several mechanisms may influence the material: (a) electric dipoles induced on FeN/C particle/tube; (b) field-induced torque on the dipoles; (c) dipole-dipole attraction; and (d) spatial redistribution of NFe/C particles/tubes in the applied field [60]. The dipole moments induced on NFe/C particles/tubes cause them to rotate, orient and move towards each other. This polarization moment leads to a fieldinduced torque T acting on particles/tubes, which is given by  $T = p \times E$ , where p is the induced dipole moments and E is the electric field. In addition to the electric field induced torque, Coulombic attraction is another force that acts on NFe/C particles/tubes, which is generated between the oppositely charges of neighbouring dipoles. Under a DC electric field, dielectrophoresis movement of particles in a fluid under the influence of an electric field can occur [61]. Polarized particles/tubes are able to migrate, rotate, orient, and move towards each other. Furthermore, the Columbic attraction could cause NFe/C particles/tubes to be adjacent to each other to produce a firmly packed layer (Figure 10). Under a DC electric field, dielectrophoresis movement of the particles in a fluid can cause the particles approaching each other and produce a more compact layer structure. As a result, the catalyst electrode will have an enhanced conductivity through the sample. The introduction of the compact layer in the catalyst electrode may improve the electron transfer between the catalyst electrode and alkaline media.



Figure 11. Comparisons of the differential conductances (in 10 S/m<sup>2</sup>) of different NFe/C

samples after applying different DC - electric field and the result of Pt/C 20 wt % sample.

The response of NFe/C(900°C) samples in an electric field is further studied using the differential conductance data, which were calculated as the differential of the current density J in the material with respect to the applied potential V that causes the current flow (Figure 11). Using a physical approach to study the differential conductance for catalytic reaction in the materials has not been explored well yet so far. Here, we implemented a numerical computational method to calculate the differential conductance (dJ/dV) of the sample from the electrochemical measurement data of electric current density J. A third order numerical differentiation method was used as follows [62]:

$$\frac{dJ}{dV} = \frac{(\Delta J_3 - 9 * \Delta J_2 + 45 * \Delta J_1)}{60 * h}$$

where  $\Delta J_1 = J(V + h) - J(V - h);$   $\Delta J_2 = J(V + 2h) - J(V - 2h);$  $\Delta J_3 = J(V + 3h) - J(V - 3h);$ 

and h is the step size between the two data points of the potential (V) in the calculation. It is noticed that the electrochemical measurement data such as those of the LSV results in Figures 8 and 9 presented strong non-linear behaviours, which indicated electrocatalytic reaction processes for the samples in the measurement range. Those strong non-linear behaviours are further registered by the strong peak structures in the extracted differential conductance results from the electrochemical LSV data (see Figure 11). Here, we may name them as "reaction peaks", which is also applicable in electrochemical studies due to their revealing features directly from LSV results, instead of running another measurement.

Especially, there is a substantial enhancement of the differential conductance in NFe/C(900  $^{\circ}$ C) [100 V/mm] sample in the potential region from 0.8 V to 1.0 V, compared to that of NFe/C(900  $^{\circ}$ C) [0 V/mm] sample without applying an electric field. As we can see from Figure 11, the reaction peak in the differential conductance of NFe/C(900  $^{\circ}$ C) [100V/mm] is shifted towards that of Pt/C by ~ 0.5 V, indicating an enhanced electrochemical performance and better conductivity of the sample. In addition, the peak height is even higher than that of Pt catalyst, indicating that electron transfer has been facilitated. As mentioned above, a uniform compact catalyst electrode can create better conductivity. Furthermore, impedance measurements were performed on the samples to compare with the differential conductance of

NFe/C(900°C) before and after applying DC electric field. (Figure S13). Our impedance finding is in agreement with our calculated differential conductance results.

# 3.3 Comparing Oxygen Electrode Activities (OEA)

To understand the catalytic performance, we further compared the oxygen electrode activity (OEA) of the samples. Here OEA is calculated as the difference between the ORR at -3 mA cm<sup>-2</sup> and OER at 10 mA cm<sup>-2</sup>, which is a common value in the literature [44, 63]. The current density of 10 mA·cm<sup>-2</sup> is the convention commonly used in the OER literature [64, 65]. Smaller OEA value indicates that the performance is closer to the ideal reversible oxygen electrode. Table 1 shows the accumulated OEA data for all the materials used in this study. We also compared the bifunctional oxygen electrode activities of our catalysts to those of several precious metal catalysts. To assess the overall oxygen electrode activity, the difference between the ORR and the OER metrics was considered. The OEA of NFe/C(900°C) was better than other NFe/C samples and compares favourably to the precious metal catalysts. The OEA of NFe/C(900°C) was 14% better than that of Pt/C 20wt%, i.e., closer to an ideal reversible oxygen electrode by a factor of 14 %. The presence of electron donating quaternary Ns, which are favourable for ORR, and high contents of electronwithdrawing functional groups (pyridinic N, C=O), which are attractive for OER.[33] These can lead to a good BOC performance of NFe/C(900 °C sample. Comparison between NFe/C(900°C) and the sample without N-doping indicates that the observed electrocatalytic performance is attributed to the incorporation of nitrogen groups in the sample [32, 66, 67].

Interestingly, there is a significant enhancement of OEA (0.92 V) after the applying an electric field polarization to NFe/C(900°C) [100 V/mm], which is a huge improvement of oxygen electrode activity, close to iridium catalyst[63] and also comparable to other catalysts [68-76]. The results demonstrate the low-cost and scalable synthesis for producing efficient carbon-based noble-metal-free oxygen catalysts for a variety of electrochemical applications. Applying an electric field to polarize the catalysts for enhancing their electrocatalytic performance can be a new path in the research realm.

Catalyst	ORR:E(V) at	OER:E(V) at	Oxygen electrode activity (OEA)
	$I = -3 \text{ mA.cm}^{-2}$	I=10 mA.cm <sup>-2</sup>	∆ (OER-ORR) : E(V) V vs. RHE
Pt/C 20wt% (Commercial)	0.84	2.01	1.17
Ir/C 20 wt% (Commecrial)*	0.69	1.61	0.92
Ru/C 20 wt% (Commecrial)*	0.61	1.62	1.01
undoped Carbon	-0.11	1.96	2.07
NFe/C (900°C)	0.73	1.75	1.02
NFe/C (950°C)	0.66	1.81	1.15
NFe/C(1000°C)	0.31	1.84	1.53
NFe/C (1100°C)	0.34	1.85	1.51
Applying DC electric field			
NFe/C (900°C) [0 V/mm]	0.73	1.75	1.02
NFe/C (900°C) [33.3 V/mm]	0.75	1.75	1
NFe/C (900°C) [66.6 V/mm]	0.78	1.75	0.97
NFe/C (900°C) [100 V/mm]	0.82	1.74	0.92

Table 1. Comparisons of Oxygen Electrode Activity

\* Reference [63]

### 4. Conclusions

We developed a new method for synthesizing nitrogen-iron functionalized carbon nanostructures through catalytic thermolysis of natural cotton fibers. Annealing the pretreated cotton fibers under ammonia at a temperature of 900°C yielded nitrogen-iron-doped carbon nanostructure with bamboo-like joints. The obtained data from the experimental measurements show that NFe/C(900°C) possess good bifunctional electrocatalytic activities towards ORR and OER, with an excellent stability in alkaline electrolyte. The improved electrocatalytic performance of NFe/C(900°C)[100V/mm] after an electric field polarization is comparable to that of the iridium catalyst. The additional effect of the applied electric field polarization is to create a dielectrophoresis phenomenon, which assisted the packing of the catalyst particles and resulted in a compact catalyst electrode. In addition, we implemented a physical approach to study the differential conductance for catalytic reaction in the materials that has not been explored well yet in the electrochemistry literature so far. The new NFe/C synthesis method using environmental friendly natural cotton and the enhanced electrocatalytic performance of the catalyst after applying electric field polarization has the potential to achieve low cost and mass production capability for synthesizing efficient bifunctional green catalyst for regenerative fuel cells and other applications.

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#### **Conversion of Hg/HgO to RHE**

Hg/HgO electrode calibration was carried in a three electrode system with Pt wires as working and counter electrode and Hg/HgO as reference electrode. Hydrogen saturated 0.1 M KOH was used as an electrolyte. Linear sweep voltammetry was performed at 1 mV/s scan rate and the potential at which current crosses zero was taken as thermodynamic potential (vs Hg/HgO) for the hydrogen electrode.

The potential at which current crosses zero is -0.95V vs Hg/HgO

So E (RHE) = E (Hg/HgO) + 0.95



Figure S1. Hg/HgO electrode calibration curve.



**Figure S2.** (a) XPS surveys of NFe/C (900°C); high-resolution XPS spectra of (b) C1s, (c) O1s, (d) N1s, and (e) Fe2p.



**Figure S3.** (a) XPS surveys of NFe/C (950°C) and high-resolution XPS spectra of (b) C1s, (c) O1s, (d) N1s, and (e) Fe2p.



**Figure S4.** (a) XPS surveys of NFe/C (1000°C) and high-resolution XPS spectra of (b) C1s, (c) O1s, (d) N1s, and (e) Fe2p.



**Figure S5.** (a) XPS surveys of NFe/C (1100°C) and high-resolution XPS spectra of (b) C1s, (c) O1s, (d) N1s, and (e) Fe2p.



Figure S6. Tafel slope of Pt/C 20 wt% and NFe/C(900°C) in ORR region.



**Figure S7. (a)** Hydrodynamic voltammograms of NFe/C(900°C) in O<sub>2</sub>-saturated 0.1 M KOH solution with various rotation rates from 500 to 2500 rotation *per minute* (rpm) at a scan rate of 10 mV/s. **(b)** Koutecky–Levich plots at different electrode potentials related to ORR region.



Figure S8. Koutecky–Levich plots of NFe/C(900°C) and NFe/C(1000°C) at 0.45V vs. RHE.



**Figure S9.** The electroactive surface area of (a) NFe/C(900°C), (b) NFe/C(950°C), (c) NFe/C(1000°C) and (d) NFe/C(1100°C) based on Randles-Sevcik equation.



**Figure S10.** Durability/stability Test : Current-time chronoamperometric responses of NFe/C(900°C) and Pt/C 20wt% on a GC electrode in (a) ORR region and (b) OER region performed in  $O_2$ -saturated 0.1 M KOH. The percentages are the reference to the initial current at time zero



**Figure S11.** Reversibility Test: LSV of forward current (blue curve) and backward current (red curve) of NFe/C(900°C) in O<sub>2</sub>-0.1 M KOH at 1600 rpm, scan rate 10 mV/s.



Figure S12. (a) The image of the electrode surface upon applying 100 V/mm (b) The image of the electrode surface after applying 180 V/mm

**Impedance measurement** [1-3]



**Figure S13.** AC impedance plots of (a) NFe/C(900°C) [100 V/mm], (b) NFe/C(900°C) [0 V/mm] at room temperature in 0.1M KOH electrolyte.

The impedance data of the samples are presented in **Figure S13.** The semicircle with a larger diameter corresponds to a higher charge transfer resistance. Hence, one can see that for the NFe/C(900°C) [100 V/mm], the semicircle displayed smaller diameter when compared to the NFe/C(900°C) [0V/mm], indicating that the charge transfer resistance was lowered by applying electric field on the sample. Moreover, for the sample after applying the electric field, the line appearing at the lower impedance region is around 45° line, implying that the diffusion process on this material was greatly strengthened since the 45° line corresponds to a Warburg diffusion process. The results indicated that the charge transfer rate was accelerated on the surface of NFe/C(900°C) [100 V/mm] after applying electric field to polarize the sample.

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