




N-doped three-dimensional carbon foam as binder-free electrode for organic pollutants removal by electro-Fenton in neutral medium

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Abstract

Electro-Fenton in neutral medium has attracted more and more attention since it can relieve the costs of H₂O₂ storage and pH adjustment, which are the major disadvantages limiting the practical applications of Fenton reaction. The electrode with good performance for electrochemical H₂O₂ production from O₂ in neutral medium is of great importance in electro-Fenton. Herein, the N-doped three-dimensional carbon foam (NCF) electrode was obtained by using melamine foam as precursor. The nitrogen functional groups and graphitization degree could be tailored by adjusting the carbonization temperature. NCF1000, the sample carbonized at 1,000 °C, presents the H₂O₂ selectivity of 81.9%, which is the highest among those of other NCFs. The H₂O₂ concentration in neutral medium on NCF1000 achieved 0.87 mmol L⁻¹ at -0.6 V, which is 1.8, 2 and 2.6 times as much as those on graphite, carbon cloth and carbon felt. Using as cathode in electro-Fenton, NCF1000 exhibits the kinetic rate of 0.062 min⁻¹ for phenol degradation, which is 4.1 times larger than that on graphite electrode. As well, the performance of NCF1000 shows no visible attenuation after ten times phenol removal experiments, demonstrating its good reusability. These results indicate the potential of NCF as a promising alternative for commercial carbon-based electrode in electro-Fenton.

Key words: electro-Fenton, N-doped carbon, neutral medium, organic pollutants control, oxygen reduction reaction

INTRODUCTION

Generating hydroxyl radicals ($\bullet\text{OH}$) from H₂O₂ for the degradation of organic pollutants, which is generally called the Fenton reaction, is one of the advanced oxidation processes and has attracted increasing attention as an effective and environmentally friendly technology (Nidheesh & Gandhimathi 2012; Hammouda *et al.* 2016; Moreira *et al.* 2017). The hydroxyl radicals are non-selective oxidants with a high oxidation potential of 2.8 eV (in the gas phase) and can react with most organic contaminants to decompose them into CO₂ and other inorganic ions (Liu *et al.* 2015a; Wang *et al.* 2015a; Xu *et al.* 2016). However, although the traditional Fenton reaction has been employed for wastewater treatment, there are still two major challenges which limit its widespread application: (1) the storage and the transportation of H₂O₂ require high safety standards and will generate extra costs, which are even higher than the costs of H₂O₂ itself (Yang *et al.* 2007; Zhang *et al.* 2011; Hammouda *et al.* 2016);

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(2) the pH of the wastewater must be adjusted to near-acidic ($\text{pH} = 2\text{--}4$), resulting in a more expensive and complicated treatment process (Nidheesh & Gandhimathi 2012).

Electro-Fenton system is an efficient technology to overcome the first challenge, as it *in situ* produces H_2O_2 by electrochemical reduction of O_2 (Jirkovský *et al.* 2011; Luo *et al.* 2015; Sklari *et al.* 2015; Perazzolo *et al.* 2015; Plakas *et al.* 2016; Zhao *et al.* 2018a). The second challenge can be solved by combining electro-Fenton technology with heterogeneous Fenton-like catalysts, which can catalyze H_2O_2 to produce $\cdot\text{OH}$ in neutral medium (Wang *et al.* 2013; Zhang *et al.* 2015a, 2015b). Thus, the electro-Fenton system in neutral medium, which can overcome both of the challenges of the traditional Fenton system, has attracted much more attention (Li *et al.* 2009; Sun *et al.* 2015; Jiang *et al.* 2016; Zhao *et al.* 2016). However, the kinetics of electrochemical reduction of O_2 in neutral medium are sluggish (Li *et al.* 2009; Liu *et al.* 2015b; Jiang *et al.* 2016), which significantly limits the efficiency of this technology, leading to a high demand for cathode electrocatalysts with good performance (Wang *et al.* 2015b; Zhao *et al.* 2018b).

Carbon-based materials have been widely used as electrodes for electrochemical H_2O_2 production from O_2 due to the good conductivity, high selectivity, good stability and low price (Khataee *et al.* 2011; Zhou *et al.* 2013; Moreira *et al.* 2014; Le *et al.* 2016). However, since the H_2O_2 production performance of these materials is poor in neutral medium, further improvement is urgently needed. Doping nitrogen atoms into carbon materials is an effective method to adjust the electrochemical properties of the carbon-based catalysts due to the different electronegativity between nitrogen and carbon (Zhang *et al.* 2008; Wei *et al.* 2014). N-doped carbon materials have been reported as catalysts with good electrochemical activity for oxygen reduction reaction (ORR) in alkaline through the four-electron pathway (Liao *et al.* 2015; Liu *et al.* 2015c; López-Salas *et al.* 2016). Interestingly, several recent works show that the selectivity of O_2 reduction on N-doped carbon materials highly depends on the types of nitrogen functional groups and the applied pH of the electrolyte (Fellinger *et al.* 2012; Lee *et al.* 2012; Park *et al.* 2014; Sheng *et al.* 2015; Noffke *et al.* 2016), suggesting a strong possibility that N-doped carbon materials could be electrocatalysts with superior performance for electrochemical H_2O_2 production from O_2 in neutral medium (Lee *et al.* 2012; Noffke *et al.* 2016).

Many methods have been developed to synthesize N-doped carbon electrode, such as chemical vapor deposition, hydrothermal, and so on (Zhang *et al.* 2008; Fellinger *et al.* 2012; Chen *et al.* 2013; Wei *et al.* 2014; Liu *et al.* 2015c). Among these methods, forming N-doped three-dimensional carbon foam by carbonizing the N-containing precursor with three-dimensional structure presents significant advantages (Lee *et al.* 2012; Chen *et al.* 2013; Sheng *et al.* 2015). The three-dimensional structure can facilitate the mass transfer, which is beneficial to enhance H_2O_2 production from O_2 reduction (Chen *et al.* 2013; Zhang *et al.* 2015c). Furthermore, the self-support electrode with absence of conductive polymer as binder has a better durability than the traditional electrode during the oxidation of pollutants in electro-Fenton system (Zhang *et al.* 2015c).

Herein, we synthesized the N-doped three-dimensional carbon foam (NCF) by simply carbonizing commercial melamine foam under Ar atmosphere and evaluated it as electrocatalyst for electrochemical production of H_2O_2 from O_2 in neutral medium. The relationship between the nitrogen functional groups and the selectivity of O_2 reduction in neutral medium was investigated. The NCF was further employed as cathode in the electro-Fenton system in neutral medium for organic pollutants' removal and its performance was compared to several commercial electrodes to evaluate its potential for practical applications. The results of this work not only provide a cheap and efficient cathode for electro-Fenton, but also contribute to the understanding of O_2 reduction mechanism on N-doped carbon in neutral medium.

EXPERIMENTAL

Materials

Melamine foam was supplied by Haohua-Junhua Group Co. Ltd, China. Carbon cloth, carbon felt, and graphite electrode were purchased from Hesen company. H_2SO_4 , NaOH, and Na_2SO_4 were supplied by Tianjin Bodi Chemical Reagent Co. Ltd. The concentration of H_2SO_4 is 18.4 mol/L (98 wt%). The NaOH and Na_2SO_4 are chemically pure. Phenol, atrazine, and bisphenol A were supplied by Aladdin company. Nafion solution was PFSA polymer dispersion D-520 with a concentration of 5 wt% from Dupont. The Nafion 117 proton exchange membrane was also purchased from Dupont.

Synthesis of N-doped three-dimensional carbon foam (NCF)

In a typical process, the melamine foam was carbonized at 800 °C with a heating rate of 5 °C min⁻¹ for 2 h under Ar atmosphere. Three obtained black samples carbonized at 650 °C, 800 °C, and 1,000 °C were named as NCF650, NCF800, and NCF1000, respectively. With heat treatment temperature of 1,100 °C, the sample collapsed and could not be used as a self-supporting electrode.

Physicochemical characterization

The Shimadzu LabX XRD-6000 was employed to reveal the X-ray diffraction (XRD) patterns. Raman spectra were recorded by Renishaw System 2000 with a wavelength of 623.8 nm (He-Ne laser excitation). Elemental mapping was measured by the Iridium Ultra Premium EDS System (A550I, IXRF, USA) for 10 minutes. VG ESCALAB 250 spectrometer was used to reveal the X-ray photoelectron spectra (XPS) of samples. Hitachi S-4800 microscope was used to record the scanning electron microscopy (SEM) images. N_2 adsorption-desorption isotherms were measured at 77 K with a Quadasorb instrument.

Electrochemical characterization

The electrochemical workstation (CHI 760E) and a three-electrode cell were employed to conduct the electrochemical tests at room temperature. The reference electrode was saturated Hg/HgO electrode (SCE) and the Pt wire was used as counter electrode. 0.1 M Na_2SO_4 was used as electrolyte for all the electrochemical measurements. The pH of the solution was adjusted by 1 M KOH and 1 M H_2SO_4 . Pure O_2 or N_2 was flowed into the solution for 0.5 h before tests to ensure the solution was saturated by O_2 or N_2 . A two-chamber reactor was used for the H_2O_2 production experiment and a one-chamber reactor with a volume of 20 mL was used for both the H_2O_2 production and pollutants' removal experiments. Both of the reactors are rectangular. The two-chamber reactor was divided by the Nafion 117 proton exchange membrane. The volume of the solution during the reaction in each chamber was 20 mL. No stirring was conducted during the production of H_2O_2 experiments. The reaction temperature was not controlled during all the experiments. However, since the room temperature of the laboratory was controlled by air conditioning and the electrochemical reactions in this work do not lead to a huge change in temperature, the reaction temperature could be the same as the room temperature, which is around 25 °C.

Cyclic voltammetry (CV) measurements were operated with the scan rate of 10 mV s⁻¹. Linear sweep voltammograms (LSVs) were collected from a rotating ring-disk electrode (RRDE) system (Pine Instrumentation, USA) with a platinum/glassy carbon RRDE at 1,600 rpm. H_2O_2 selectivity was calculated from the following equation (Lee *et al.* 2012; Park *et al.* 2014):

$$\text{H}_2\text{O}_2\% = (200 \times I_r/N)/(I_r/N + I_d) \quad (1)$$

where I_r and I_d were the disk current and ring current, respectively. The N was 0.37, which was the collection efficiency of Pt ring. The current efficiency was calculated by the following equation:

$$CE = 100\% \times nFCV/It \quad (2)$$

where n is the electron number, F is the Faraday constant (96,485 C/mol), C is the concentration of H_2O_2 , V is the solution volume, I is the current, and t is the time. The electro-Fenton treatment of pollutants and H_2O_2 production were measured with the effective working electrode area of 4 cm^2 (rectangular, $2 \text{ cm} \times 2 \text{ cm}$). The working electrode was facing the counter-electrode and the distance between the electrodes was 2.5 cm. A 20 mL solution of 20 mg L^{-1} pollutants (phenol, atrazine or bisphenol A) was used as electrolyte. Commercial $FeOOH$ was used as Fenton reagent during the process and the solution was stirred by magnetic stirrer with the speed of 600 rpm. The flow rate of O_2 was 300 mL/min. The illustration of the experimental apparatus can be seen in Figure 1.

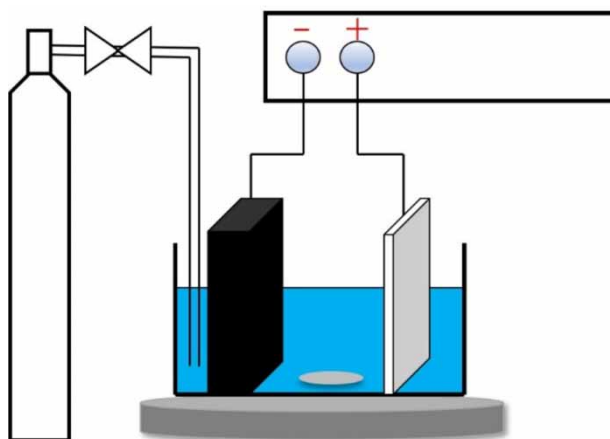


Figure 1 | Illustration of the experimental apparatus.

Analytical methods

H_2O_2 concentration was analyzed by the flow-injection chemiluminescence method (MIP-B, Xi'an Remex, China). The Waters 2695, high-performance liquid chromatography, was employed to investigate the concentration of phenol, bisphenol A and atrazine. The multi N/C2100S (Analytikjena, Germany) was employed to measure the total organic carbon (TOC). The chemical oxygen demand (COD) was monitored according to the standard method of China. Electron paramagnetic resonance (EPR) spectrometer was employed to identify reactive species during the electro-Fenton process (300E, Bruker, Germany). 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was chosen as the spin trap agent.

RESULTS AND DISCUSSION

Characterizations of NCF electrode

As shown in Figure 2(a), the melamine foam was successfully transformed into black NCF after the carbonization process. SEM images (Figure 2(b) and 2(c)) show the three-dimensional structure of the NCF1000, and the strut of the foam has a diameter of $1.5\text{--}2 \mu\text{m}$. The samples kept the foam

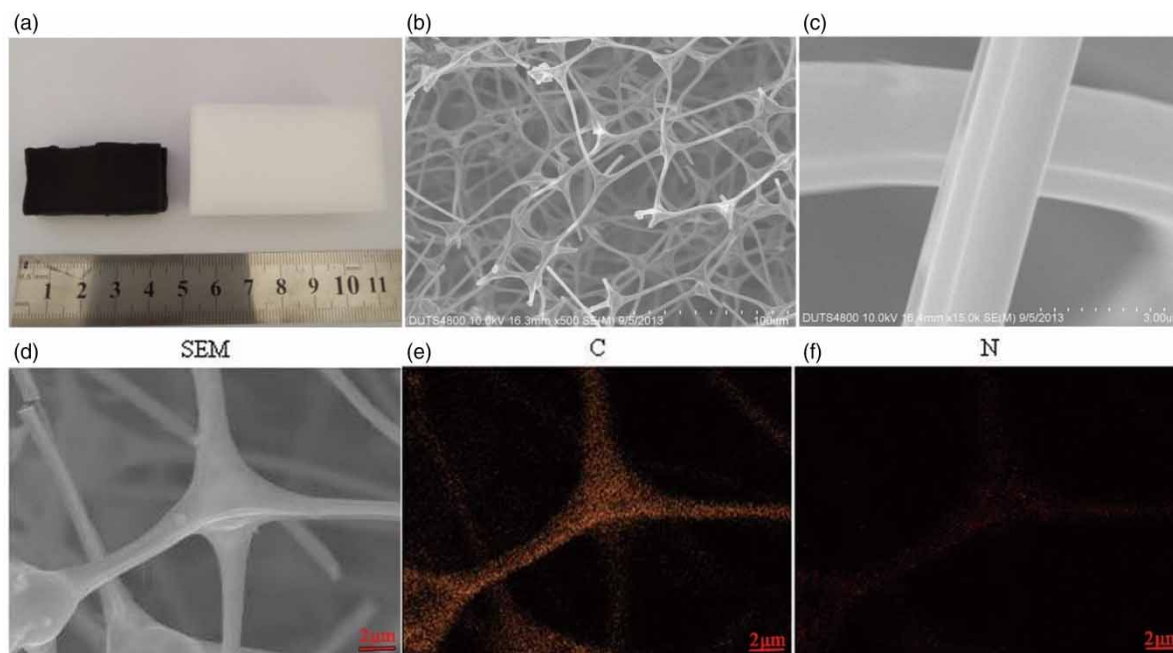


Figure 2 | (a) Photograph of NCF and melamine foam, (b and c) SEM images of NCF1000, the EDS mapping scan of (d) the SEM image of NCF1000, (e) C element of NCF1000, (f) N element of NCF1000.

structure and can be used as electrode without any conductive binder. EDS mapping scan is shown in Figure 2(d)–2(f). It reveals that C and N are uniformly distributed in the sample.

XRD patterns of NCF650, NCF800, and NCF1000 are shown in Figure 3(a). The broad peak centered at 26° represents the C (002) facet, demonstrating the successful transformation of melamine to graphitic carbon during the carbonization. With a higher carbonization temperature, the C (002) peak becomes narrow and the peak located at 43° corresponding to the C (100) facet could be found in the patterns of NCF800 and NCF1000. The results reveal that higher carbonization temperature leads to higher graphitization degree. Raman spectra of the three samples present the D band peak located at $1,350\text{ cm}^{-1}$ and the G band peak located at $1,580\text{ cm}^{-1}$ (Figure 3(b)). Generally, lower D/G peak intensity ratio (I_D/I_G) reveals less disordered atoms in graphitic carbon. The I_D/I_G values for NCF650, NCF800, and NCF1000 are 1.16, 1.07, and 1.02, respectively. The sample with higher

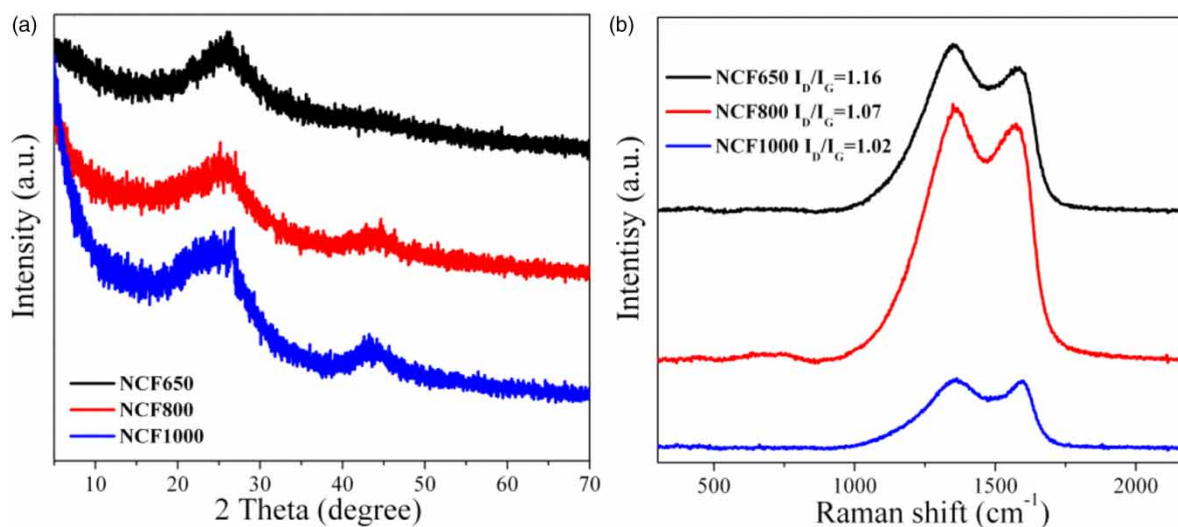


Figure 3 | (a) The XRD patterns and (b) the Raman spectra of NCF650, NCF800, and NCF1000.

carbonization temperature shows a decreased I_D/I_G value, indicating that the higher carbonization temperature leads to higher graphitization degree, in accordance with XRD results.

It is known that the nitrogen functional groups are vital with respect to H_2O_2 generation by ORR on N-doped carbons. Table 1 shows the elemental compositions of NCF650, NCF800, and NCF1000 investigated by XPS. The peaks representing C 1s, O 1s, and N 1s were discovered by the full survey spectra (Figure S1). The C contents increased by increasing the carbonization temperature, while the N and O contents decreased significantly. High-resolution C 1s spectra of NCF650, NCF800, and NCF1000 is shown in Figure 4(a). The peak located at 284.6 eV corresponds to the C=C bond and its intensity and shape are highly correlated with the graphitization degree. Significantly, NCF1000 presents the highest graphitization degree among all the samples, which could be attributed to its highest carbonization temperature. High-resolution N 1s spectra of three samples were deconvoluted into four peaks located at 398.1, 399.2, 401.2, and 402.4 eV, corresponding to pyridinic-N, pyrrolic-N, graphitic-N, and oxidized-N, respectively (Figure 4(b)–4(d)). Due to the relative

Table 1 | The XPS element contents of NCF650, NCF800, and NCF1000

Sample	C (at%)	N (at%)	O (at%)	Na (at%)
NCF650	63.60%	7.55%	18.39%	10.46%
NCF800	71.59%	4.99%	15.92%	7.50%
NCF1000	91.49%	2.62%	4.73%	1.16%

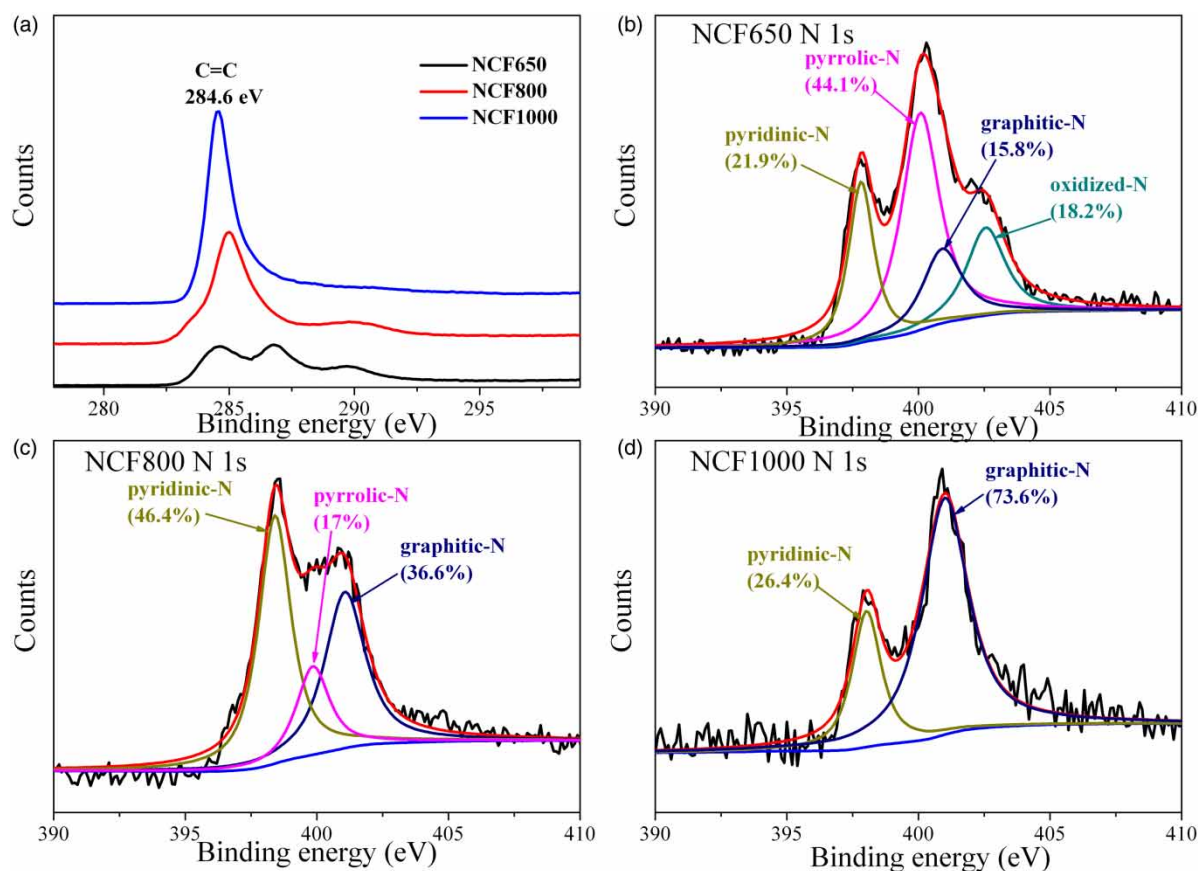


Figure 4 | (a) High-resolution XPS C 1s spectra of NCF650, NCF800, and NCF1000, the high-resolution XPS N 1s spectra of (b) NCF650, (c) NCF800, and (d) NCF1000.

low carbonization temperature, NCF650 exhibits the lowest C content of only 63.60% and highest N content of 7.55%. However, NCF650 contains large amounts of pyrrolic-N (44.1% of total N) and oxidized-N (18.2% of total N), both of which are considered as non-active nitrogen functional groups with respect to ORR. NCF800, the sample with higher carbonization temperature than NCF650, presents a lower pyrrolic-N content of just 17.0% of total N and the peak corresponding to oxidized-N disappeared. NCF1000 with the highest carbonization temperature even shows an absence of pyrrolic-N. The graphitic-N proportion content of NCF1000 is 73.6% of total N, which is remarkably higher than those of NCF800 (36.6% of total N) and NCF650 (15.8% of total N). The higher graphitic-N proportion of NCF1000 could be ascribed to the higher graphitization degree caused by the higher carbonization temperature. The results indicate that the nitrogen functional groups of NCFs can be tailored by adjusting the carbonization temperature.

Electrochemical oxygen reduction performance of NCF

The ORR performance of NCFs was first examined by CV experiments. All three samples were used as self-supporting cathodes without any current collector. CV curves for NCF650, NCF800, and NCF1000 were measured in N_2 or O_2 saturated 0.1 M Na_2SO_4 solution (Figure 5). Compared to the CV curves recorded in N_2 -saturated solution, the CV curves of all the samples in O_2 -saturated solution present significantly larger electrochemical reduction current, demonstrating that NCF650, NCF800, and NCF1000 have the ability to electrochemically reduce oxygen. At -1.0 V, the ORR

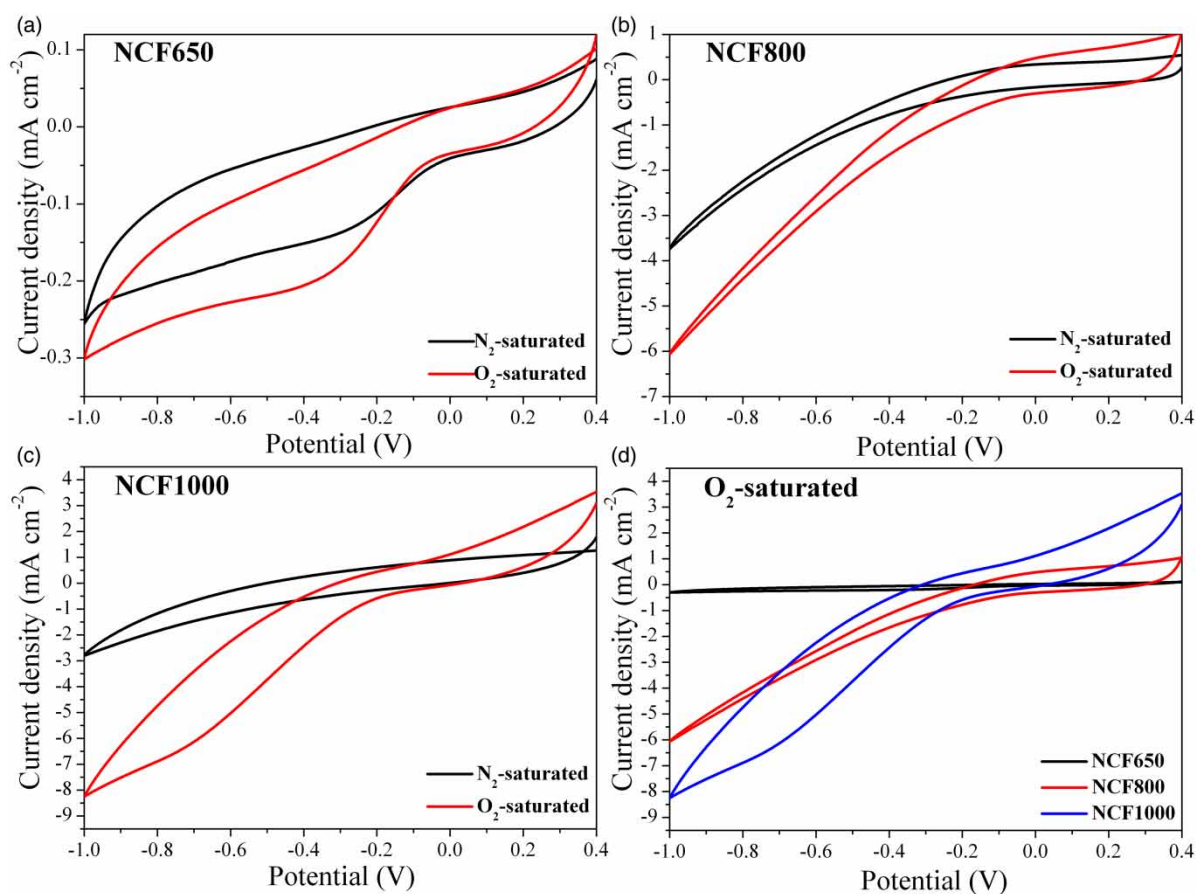


Figure 5 | CV curves of (a) NCF650, (b) NCF800, and (c) NCF1000 in N_2 -saturated and O_2 -saturated solution, (d) CV curves of NCF650, NCF800, and NCF1000 in O_2 -saturated solution; electrolyte: 0.1 M Na_2SO_4 , pH = 7, scan rate: 10 mV/s, temperature = 25 °C.

current density for NCF650, NCF800, and NCF1000 is 0.05, 2.5, and 5.4 mA cm⁻², respectively. NCF1000 shows larger ORR current density than other NCFs.

It is known that the O₂ can be reduced through two pathways: two-electron pathway and four-electron pathway (Equations (3) and (4)). Thus, the high selectivity towards the two-electron pathway, which will generate H₂O₂, is highly demanded for the cathode in the electro-Fenton system:



ORR rotating ring-disk electrode (RRDE) system was employed to further investigate the ORR activity and H₂O₂ selectivity of NCFs. The samples were ground into powder and mixed with Nafion solution (the concentration is 0.5%, diluted by water) to prepare the working electrode. The working electrode was dried at 30 °C overnight. Since the pH of the solution may influence the H₂O₂ selectivity in ORR, the solutions with the pH range from 6 to 9 were employed in the experiments (Figure 6). It could be noticed that NCF1000 exhibits both the largest ring current density and the largest disk current density at pH 6–9, indicating its best ORR activity. As well, NCF800 shows better activity than NCF650. Taking the XPS results into consideration, the highest ORR activity of NCF1000 could be ascribed to the high proportion content of pyridinic-N and graphitic-N, both of which have been implied as active sites for ORR by other reports.

To be used as an effective cathode in the electro-Fenton process, the electrode should have not only good ORR activity, but also good H₂O₂ selectivity. Based on the RRDE results, the H₂O₂ selectivity of

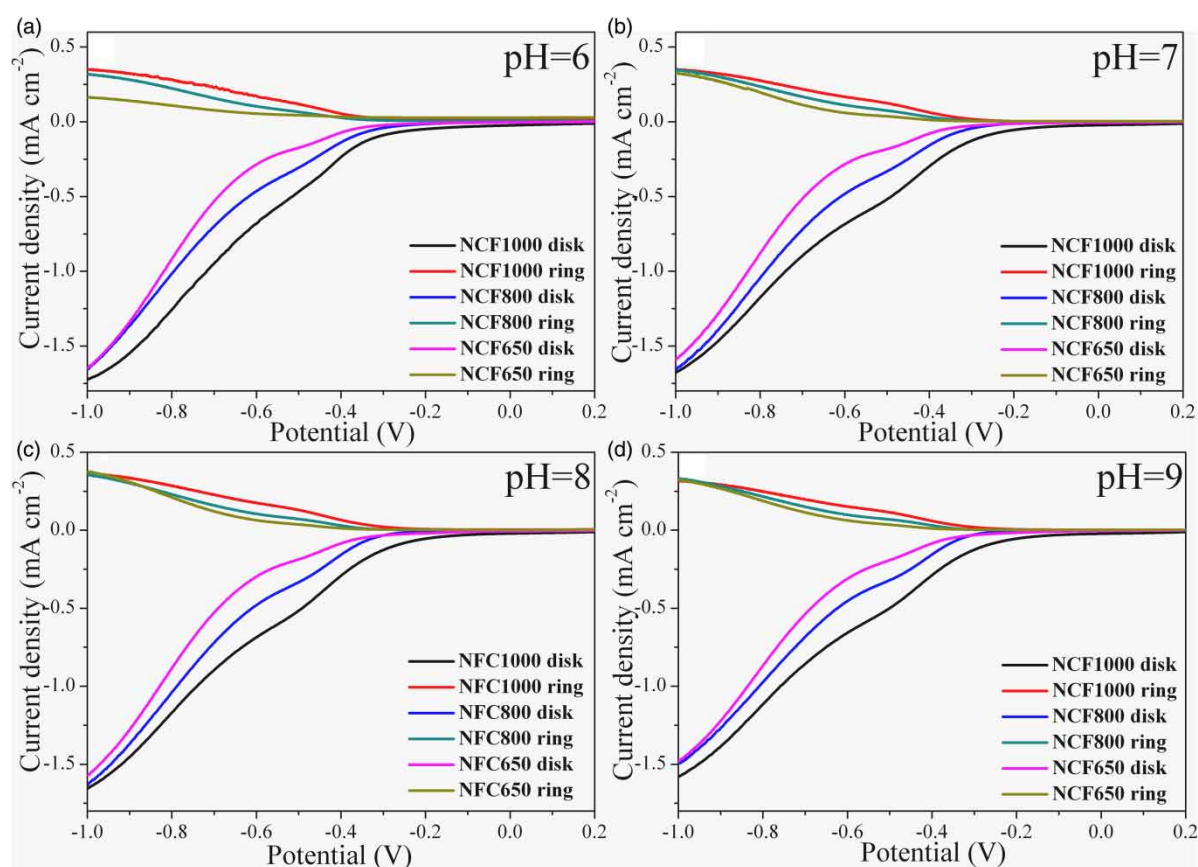


Figure 6 | (a–d) LSVs of NCF650, NCF800, and NCF1000 on RRDE in the O₂-saturated solution at (a) pH = 6, (b) pH = 7, (c) pH = 8, and (d) pH = 9, respectively; electrolyte: 0.1 M Na₂SO₄, scan rate: 10 mV/s, temperature = 25 °C.

NCF1000 and NCF800 were calculated and shown in Table 2. The highest H_2O_2 selectivity of NCF1000 is 81.9% while that of NCF800 is 78.0%. At pH 6–9, the H_2O_2 selectivity of NCF1000 remained above 70% and was even higher than recently reported N-doped graphene (75.9%) in pH 7 (Su *et al.* 2019), indicating that it can be used as cathode for H_2O_2 generation in neutral medium. Remarkably, both NCF1000 and NCF800 present the highest H_2O_2 selectivity at -0.6 V . H_2O_2 selectivity decreased with the applied potential negative shift, revealing -0.6 V may be the optimized working potential.

Table 2 | $S_{\text{H}_2\text{O}_2}$ of NCF800 and NCF1000 at pH = 6–9 and different potentials

Sample	$S_{\text{H}_2\text{O}_2}$ at -0.4 V	$S_{\text{H}_2\text{O}_2}$ at -0.6 V	$S_{\text{H}_2\text{O}_2}$ at -0.8 V	$S_{\text{H}_2\text{O}_2}$ at -1.0 V
NCF1000 pH = 6	77.3%	81.8%	75.6%	71.9%
NCF1000 pH = 7	72.8%	79.8%	77.4%	71.9%
NCF1000 pH = 8	75.7%	81.9%	79.5%	75.0%
NCF1000 pH = 9	71.8%	76.9%	75.4%	70.4%
NCF800 pH = 6	71.7%	78.0%	77.4%	70.8%
NCF800 pH = 7	71.0%	77.0%	76.1%	72.3%
NCF800 pH = 8	68.3%	74.5%	75.1%	74.1%
NCF800 pH = 9	69.9%	74.3%	74.8%	75.1%

Based on all the experiment results above, it is suggested N-doped carbons could electrochemically reduce oxygen to H_2O_2 in neutral medium and NCFs show the potential to be used as cathode in the electro-Fenton system in neutral medium.

Electrochemical H_2O_2 generation on NCF

The H_2O_2 generation tests were conducted in a two-chamber reaction with a proton exchange membrane. The working potential was -0.6 V and the initial pH was 7. Figure 7 shows the H_2O_2 concentration and the current efficiency for H_2O_2 production on all three samples. Significantly, the NCF1000 displayed higher H_2O_2 generation rate than those of NCF800 and NCF650. The current efficiency for H_2O_2 production on NCF1000 at 5 min, 10 min, and 15 min was 76.4%, 73.7%, and

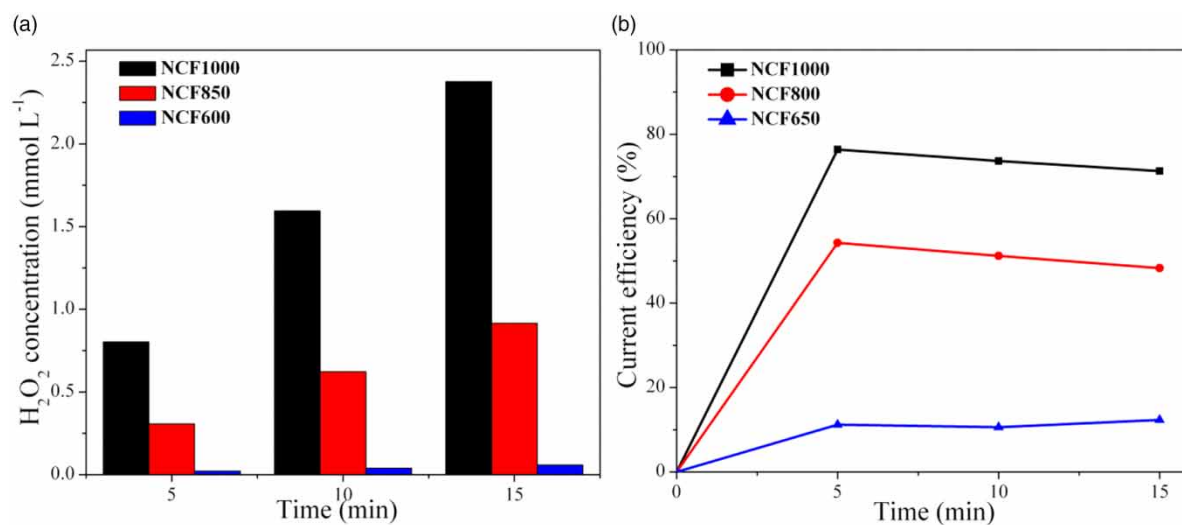


Figure 7 | (a) H_2O_2 concentration and (b) current efficiency of NCF650, NCF800, and NCF1000 for H_2O_2 production in a two-chamber reactor; electrolyte: 0.1 M Na_2SO_4 , pH = 7, working potential: -0.6 V , O_2 flow rate: 300 mL/min, temperature = 25 °C.

71.3%, which were close to the RRDE results. However, the current efficiency for H_2O_2 production on NCF800 was 54.3%–48.3%, which is significantly lower than the H_2O_2 selectivity calculated from RRDE results. As well, NCF650 only presents the current efficiency for H_2O_2 production of 12.2%–10.4%. Since the NCFs were used as self-supporting cathodes without any current collector or binder, the low current efficiency of NCF650 and NCF800 could be due to the poor conductivity resulting from the relatively low graphitization degree. Thus, NCF1000 is the sample with the best H_2O_2 production performance among all the samples. Furthermore, the performance of NCF1000 was also compared to those of the cathodes reported by current literature (Table S1). It can be noticed that the NCF1000 shows higher CE than other carbon-based materials, such as hierarchically porous carbon and graphene (Zhang *et al.* 2018; Yu *et al.* 2019), demonstrating its superior performance in neutral medium.

To evaluate the potential ability of NCF1000 as cathode in electro-Fenton system, H_2O_2 production on NCF1000 was conducted in a one-chamber reactor at working potential of -0.4 V to -0.8 V under pH 7 (Figure 8). The H_2O_2 concentration achieved the max concentration at 60 min of electrolysis, which might be caused by the decomposition of H_2O_2 on the anode in the one-chamber reactor. The highest H_2O_2 concentration on NCF1000 was 0.87 mmol L^{-1} while the working potential was -0.6 V. Thus, -0.6 V was the optimized working potential and therefore was applied in the following experiments.

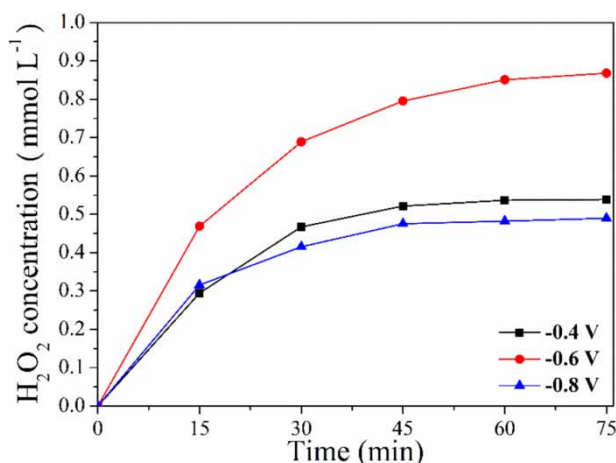


Figure 8 | H_2O_2 concentration curves of NCF1000 at different working potentials; electrolyte: 0.1 M Na_2SO_4 , pH = 7, O_2 flow rate: 300 mL/min, temperature = 25 °C.

The H_2O_2 generation on NCF1000 at pH 6–9 was also tested to evaluate the performance of NCF1000 in neutral medium (Figure S2). It can be noticed that the H_2O_2 concentration on NCF1000 remained stable, demonstrating that the NCF1000 could electrochemically reduce oxygen to H_2O_2 in the neutral solution at pH 6–9.

For comparison, the performances of graphite electrode, carbon cloth, and carbon felt for electro-Fenton were also tested under the same condition. The properties of these electrodes can be seen in Table S2. As shown in Figure 9, the H_2O_2 concentration on NCF1000 at 60 min was 1.8 times as much as that on graphite, 2 times as much as that on carbon cloth, and 2.6 times as much as that on carbon felt. NCF1000 exhibits significantly better H_2O_2 generation performance than these commercial materials, indicating its potential ability to be used as the cathode in the electro-Fenton system for wastewater treatment.

The origin of the better H_2O_2 generation performance of NCF1000 compared to other commercial carbon-based materials was further discussed. First, due to the high carbonization temperature and the N-containing precursor, the NCF1000 presents 73.6% graphitic-N of total N and high

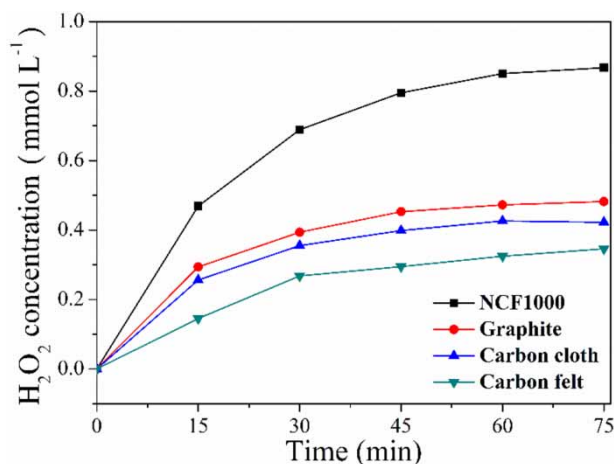


Figure 9 | H₂O₂ concentration curves of NCF1000, graphite, carbon cloth, and carbon felt at -0.6 V in one-chamber reactor; electrolyte: 0.1 M Na₂SO₄, pH = 7, O₂ flow rate: 300 mL/min, temperature = 25 °C.

graphitization degree, both of which result in the chemically active sites on NCF1000 for O₂ reduction. Second, the three-dimensional structure of the NCF1000 may lead to a large surface area, which will facilitate the mass transfer. To further reveal the morphology of NCF1000, the N₂ adsorption-desorption isotherm of NCF1000 was measured to investigate the Brunauer-Emmett-Teller (BET) surface area and the pore-size distribution (Figure S3). The BET surface area and total pore volume of NCF1000 are $1,343$ m²/g and 0.235 cm³/g, respectively. The large BET surface area may contribute to the better H₂O₂ generation performance of NCF1000.

Removal of organic pollutants on NCF

To evaluate the electron-Fenton performance on NCF1000 in neutral medium, simulated phenol wastewater with an initial phenol concentration of 20 mg L⁻¹ was treated by NCF1000. For comparison, the graphite electrode was also tested under the same condition. Commercial FeOOH was selected as the Fenton-like catalyst and the loading mass was 0.5 g L⁻¹. As shown in Figure 10(a), without the presence of O₂, the phenol removal efficiency on NCF1000 in 60 min was only 30%.

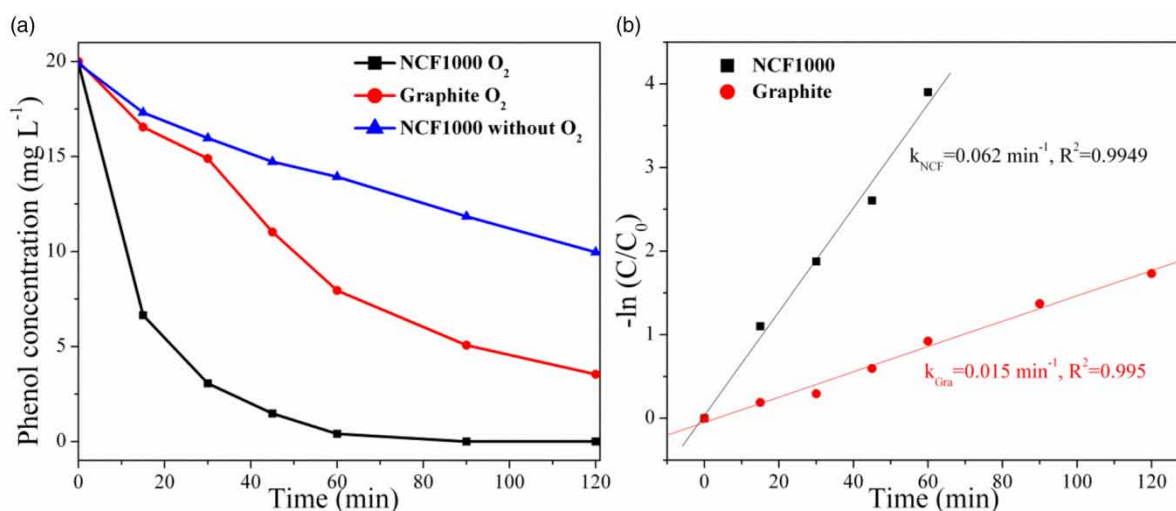


Figure 10 | (a) Phenol removal of NCF-1000 with O₂, NCF-1000 without O₂ and, graphite with O₂, and (b) kinetics curves of NCF-1000 and graphite for phenol removal; electrolyte: 0.1 M Na₂SO₄, pH = 7, O₂ flow rate: 300 mL/min, working potential: -0.6 V, initial phenol concentration: 20 mg/L, FeOOH dosage: 0.5 g/L, temperature = 25 °C.

However, the NCF1000 as cathode in O_2 -saturated solution can remove 98% of phenol in 60 min. These results indicate the highly efficient removal of phenol could be attributed to catalytic electro-Fenton process. Moreover, with commercial graphite as cathode, the process can only remove 60% of phenol in 60 min. The apparent rate constant for phenol removal on NCF1000 was 0.062 min^{-1} , which is 4.1 times higher than that of commercial graphite electrode. Recently reported studies for phenol degradation in neutral medium can be seen in Table S3; the performance of NCF1000 is comparable to some reported studies. The mineralization of phenol on NCF1000 and graphite was also evaluated. As shown in Figure 11, the TOC removal efficiency of 68% was achieved on NCF1000 after 5 h reaction while the TOC removal efficiency on the graphite electrode was just 44% at a similar reaction time. These results reveal that NCF1000 demonstrates the better performance as cathode in the electro-Fenton system than graphite electrode, demonstrating the practical potential of NCF1000.

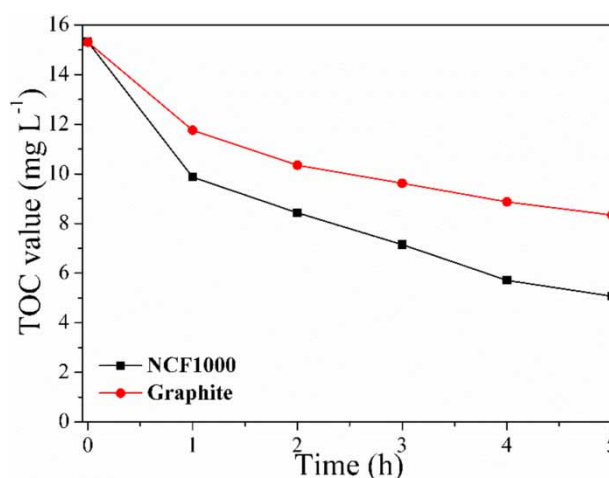


Figure 11 | TOC removal on NCF1000 and graphite; electrolyte: 0.1 M Na_2SO_4 , pH = 7, O_2 flow rate: 300 mL/min, working potential: -0.6 V , initial phenol concentration: 20 mg/L, $FeOOH$ dosage: 0.5 g/L, temperature = 25 °C.

To investigate the origin of the good phenol removal performance on NCF1000, EPR tests were conducted in the absence of pollutants. First, the test with NCF1000 as cathode at -0.6 V was measured in N_2 -saturated solution and no signal of any radicals was found in the curve, as shown in Figure 12.

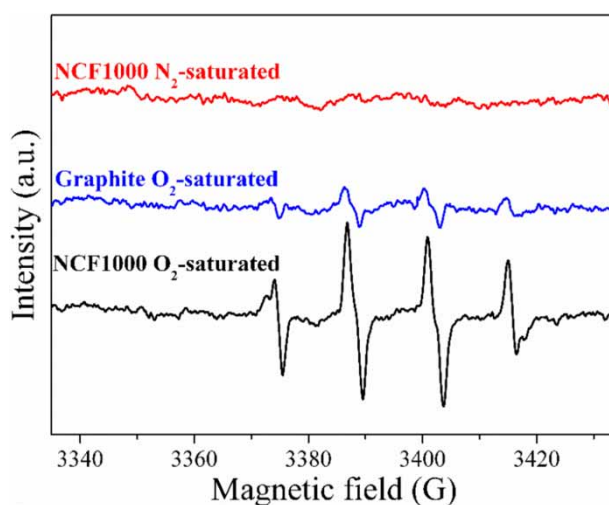


Figure 12 | EPR curves of NCF1000 and graphite in N_2 -saturated or O_2 -saturated solution; electrolyte: 0.1 M Na_2SO_4 , pH = 7, O_2 flow rate: 300 mL/min, working potential: -0.6 V , $FeOOH$ dosage: 0.5 g/L, temperature = 25 °C.

Then, the electrolyte was replaced by O_2 -saturated solution and the four-fold peak with an intensity ratio of 1:2:2:1 was observed, which corresponds to the DMPO-OH signal. This result indicates that $\cdot OH$ plays a vital role in the enhanced performance on NCF1000 in O_2 -saturated solution. Furthermore, the graphite electrode was also tested and the intensity of the peak was much lower than that of NCF1000. Thus, the better performance of NCF1000 compared to graphite could be attributed to the larger amount of $\cdot OH$, which results from the higher H_2O_2 concentration produced by NCF1000.

The reusability of NCF1000 was evaluated by repeating the treatment for ten times at -0.6 V and $pH = 7$ with 0.5 g L^{-1} of $FeOOH$. As shown in Figure 13, the phenol removal efficiency on NCF1000 after ten times' treatment shows no visible attenuation, demonstrating the good reusability of NCF1000.

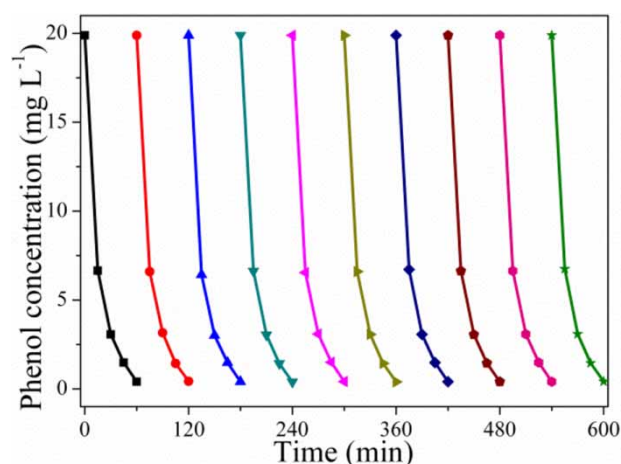


Figure 13 | Phenol removal on NCF1000 for ten times; electrolyte: 0.1 M Na_2SO_4 , $pH = 7$, O_2 flow rate: 300 mL/min, working potential: -0.6 V, initial phenol concentration: 20 mg/L, $FeOOH$ dosage: 0.5 g/L, temperature = 25 °C.

The electro-Fenton system in neutral solution can be used to remove various organic pollutants from wastewater. To evaluate the feasibility of NCF1000 as cathode in the electro-Fenton system for various organic pollutants' removal, atrazine and bisphenol A were selected as target pollutants to conduct the experiments. The concentration of both atrazine and bisphenol A was 20 mg L^{-1} . Graphite electrode was also tested as a counterpart and all the experiments were conducted at optimal conditions (-0.6 V, pH 7, 0.5 g L^{-1} $FeOOH$, 0.1 M Na_2SO_4 with O_2 -saturated). As shown in Figure 14, 97% of the bisphenol A could be removed by electro-Fenton system with NCF1000 as cathode after 150 min treatment, whereas the bisphenol A removal efficiency on graphite electrode was just 85%. After 180 min treatment, the atrazine removal efficiency on NCF1000 was 91% while the electro-Fenton system with graphite as cathode could only achieve a removal efficiency of 79%. The results demonstrate that NCF1000 as cathode in the electro-Fenton system in neutral medium exhibits better pollutants' removal performance than commercial graphite electrode for the treatment of various organic pollutants.

The real wastewater was also treated by the electro-Fenton process with NCF1000 as cathode. Real secondary effluent of refinery wastewater with COD value of 94 mg/L was received from a local factory. Since the conductivity of the wastewater was 2.06 mS/cm and the pH was 7.7 , the wastewater was directly used in the treatment without adding chemicals to adjust the pH or improve the conductivity. The other treatment conditions were the same as those in the above experiments. As shown in Figure S4, after 6 h reaction, NCF1000 achieved a COD value of 45 mg/L, which is lower than that of graphite electrode (58 mg/L) and also lower than the limit of wastewater discharge in China (GB 18918-2002, 50 mg/L). This result indicated the better performance of NCF1000 over that of commercial graphite in real wastewater treatment.

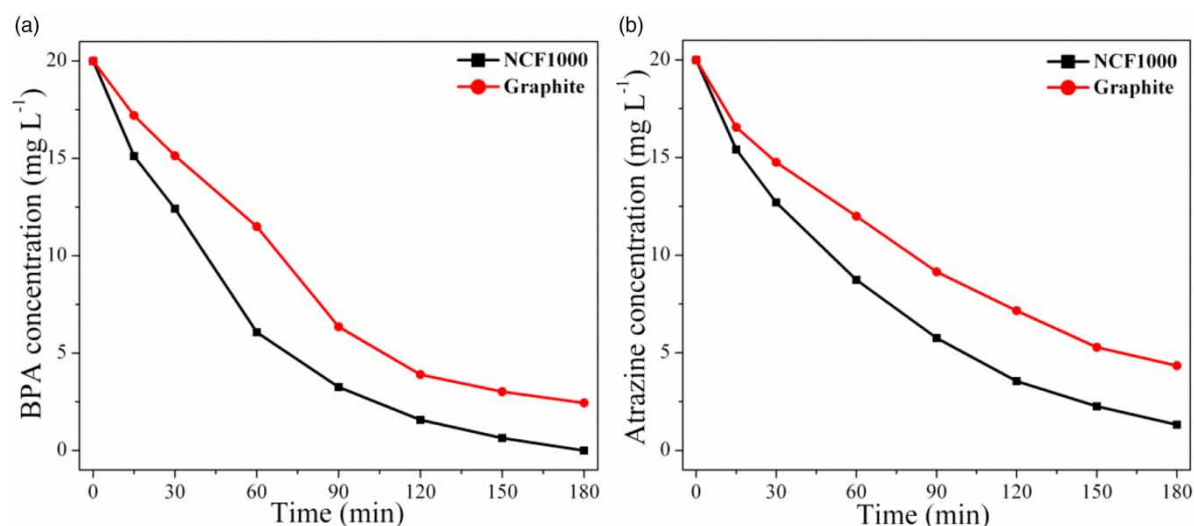


Figure 14 | Electro-Fenton removal of (a) bisphenol A and (b) atrazine; electrolyte: 0.1 M Na₂SO₄, pH = 7, O₂ flow rate: 300 mL/min, working potential: -0.6 V, initial pollutant concentration: 20 mg/L, FeOOH dosage: 0.5 g/L, temperature = 25 °C.

CONCLUSIONS

N-doped three-dimensional carbon foam electrode was prepared by carbonizing melamine foam under Ar atmosphere and it showed good performance as the cathode in the electro-Fenton system for organic pollutants' removal in neutral medium. NCF1000, the sample carbonized at 1,000 °C, presents the best activity and selectivity of H₂O₂ production among all the NCFs and several commercial electrodes. Used as the cathode in the electro-Fenton system in neutral medium, NCF1000 exhibits phenol removal kinetic rate of 0.062 min⁻¹, which is 4.1 times larger than that of commercial graphite electrode. NCF1000 also shows better performance than graphite for atrazine and bisphenol A removal. The enhanced performance could be attributed to the high yield of H₂O₂ production on NCF1000 in neutral medium, which may result from the three-dimensional structure, high graphitization degree, and the high proportion contents of pyridinic-N and graphitic-N. This work provides a new insight into the design of highly efficient and low-cost electrodes for the electro-Fenton system in neutral medium.

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