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Chemically modified graphite felt as an efficient cathode in electro-Fenton for *p*-nitrophenol degradation

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A B S T R A C T

A simple method with low-cost chemical reagents ethanol and hydrazine hydrate was used to modify graphite felt as the cathode for electro-Fenton (EF) application, using *p*-nitrophenol (*p*-Np) as the model pollutant. Characterized by scanning electron microscope, contact angle, Raman spectrum and X-ray photoelectron spectroscopy, the morphology and surface physicochemical properties after modification were observed considerably changed. After modification, some nanoparticles and oxygen and nitrogen-containing functional groups appeared on the cathode surface, which greatly improved the surface hydrophilic property and the electrocatalytic activity for oxygen reduction reaction. The effects led to the hydrogen peroxide accumulation on the modified cathode markedly increased to 175.8 mg L⁻¹, while that on the unmodified one was only 67.5 mg L⁻¹. *p*-Np of initial 50 mg L⁻¹ could be completely removed by EF using the modified cathode, and the mineralization ratio reached 51.4%, more than 2 times of the pristine one. After 10 cycles, the mineralization ratio of the modified cathode was still above 45%, suggesting that the modification method can provide an effective approach to improve EF performance, and thus benefits to promote its environmental applications.

Keywords:

Chemical modification
Hydrazine hydrate
Graphite felt cathode
Electro-Fenton
p-Nitrophenol degradation

1. Introduction

As an environmentally friendly electrochemical technology, electro-Fenton (EF) process is a promising and efficient method for degradation of refractory pollutants in aquatic environment [1,2]. Due to the continuous in-situ electrochemical generation of hydrogen peroxide from oxygen reduction reaction (ORR) (eq.1),



This process can eliminate the limits of acquisition, shipment and storage of H₂O₂, and further produces powerful oxidant ·OH with the addition of iron catalyst (eq. 2),



Theoretically the performance of the effective destruction of pollutants in EF system is substantially dependent on the generated

H₂O₂ concentration, thus an ideal cathode with high production of H₂O₂ is vital and becomes one major concern in this area.

Carbonaceous materials are the most widely used cathodes account for the merits such as no toxicity, good stability, conductivity and chemical resistance [1]. Till now, graphite [3], reticulated vitreous carbon [4], activate carbon fiber [5], carbon sponge [6], carbon/graphite felt [7,8] and carbon/PTFE composite electrode [9,10] have been reported in EF system. Among all these materials, carbon/graphite felt has outstanding advantages such as high specific surface area, good mechanical integrity, commercial availability and efficient cathodic regeneration of Fe²⁺ (eq. 3) [8,11], which make it an attractive cathode material for EF process.



To further improve the electrocatalytic activity of these carbonaceous materials, various attempts such as plasma pretreatment have been made for a more efficient H₂O₂ production [12–15]. The surface area, surface functional groups and degree of graphitization vary with the different modified processes. Chemical modification is an efficient way to improve the electrochemical activity of carbonaceous electrodes by changing their surface physicochemical

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and catalytic properties [16]. Previous literatures indicated that the oxygen-containing functional groups could induce a higher electrical conductivity and electrocatalytic activity by improving the hydrophilicity of the carbon surface [13,17,18]. And in nitrogen doped carbons, the strong electron donor behavior of N could improve the electron transfer rate of the carbons during electrocatalysis and the ORR activity [14,19,20]. Therefore, the introduction of the oxygen- or nitrogen-containing functional groups into carbonaceous materials would be an efficient way to promote the cathodic reduction of H₂O₂, and thus improve the electrochemical performance of EF system. In our previous work, a simple and efficient chemical modification method with low-cost chemical reagents ethanol and hydrazine was firstly used to modify graphite felt, and after parameters optimization the yield of H₂O₂ could be significantly increased by 160% compared with the unmodified one [21].

The objective of this work was to further validate its feasibility in activity and stability, and more importantly, to disclose why the electrochemical activity could be greatly improved by observation the changes on physicochemical and electrochemical surface properties. The performance of the modified electrodes was evaluated by the H₂O₂ production and the degradation efficiency of organic pollutant in EF system, using *p*-nitrophenol (*p*-Np) as the model target. To further enlighten the possible modification mechanism for cathode material, the morphology and surface physicochemical properties were characterized by scanning electron microscope (SEM), contact angle, Raman spectrum and X-ray photoelectron spectroscopy (XPS), and the electrochemical responses toward ORR were measured by cyclic voltammetry.

2. Experimental

2.1. Chemical modification of cathode

All chemicals used were analytical grade and used without further purification, except as noted in this study. The commercial graphite felt (Shanghai Qijie Carbon Material Co., LTD) with a specific surface area of about 0.6 m² g⁻¹ was degreased in an ultrasonic bath with acetone and deionized water in sequence, dried at 80 °C for 24h, and then heated at 150 °C for 2h. These pretreated materials were marked as CF. The pretreated graphite felts were separately immersed in 100 mL reagent solution: (A) absolute ethanol (C₂H₅OH), or (B) a mixture composed of ethanol and hydrazine hydrate (N₂H₄·H₂O) with the volume ratio of 90/10, and after refluxing at 60 °C for 6h in a water bath, the graphite felts were heated in the enclosed glass dish at 150 °C for 2h, respectively. These modified samples were marked as CF-A and CF-B, respectively.

2.2. Electrode characterization

For a morphology characterization of graphite felt cathode, a field-emission scanning electron microscopy (FE-SEM, LEO1530VP) was used. The contact angle of water on the material surface was examined by a contact angle meter (OCA15, Dataphysics). The surface elemental composition of the as-prepared samples was determined by XPS (Perkin-Elmer, a RBD upgraded PHI-5000C ESCA system, Physical Electronics, USA) with Mg K α radiation ($h\nu = 1253.6$ eV). Binding energies were calibrated by using the containment carbon (C1s = 284.8 eV). The Raman spectrum of the samples was recorded by Raman microscope system (Renishaw, System 2000) with Ar ion laser ($\lambda = 514$ nm), and the diameter of the laser spot on the sample surface was 1 μ m for the fully focused laser beam. Electrochemical measurements were carried out with a CHI660D electrochemical workstation (CH Instruments, Chenhua,

Shanghai, China) in a three-electrode cell system at a scan rate of 10 mV·s⁻¹ at ambient temperature, using the prepared cathode (5 cm × 2 cm × 0.5 cm) as the working electrode, a platinum wire as counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

2.3. Electrochemical generation of H₂O₂

The H₂O₂ electro-generation experiments were performed in a 0.13 L undivided three-electrode cell using CHI660D electrochemical workstation as stated above. The distance between the working electrode and counter electrode was 3.5 cm. Prior to the electrolysis, oxygen (96% purity) was bubbled through a small aerator near the cathode in the 0.05 M Na₂SO₄ aqueous solutions for 10 min, and then oxygen bubbled at a constant flow rate of 0.4 L min⁻¹ was reduced at a desired potential of -0.65 V (vs. SCE) on the working electrode for 120 min, with a constant magnetic stirring of 300 rpm. The electro-generated concentration of H₂O₂ was monitored by UV-vis spectrophotometer (UV759, Shanghai instrument analysis instrument Co., LTD) using the potassium titanium (IV) oxalate method [21]. The current efficiency (CE) of H₂O₂ production, defined as the ratio of the electricity consumed by the electrode reaction of interest over the total electricity passed through the circuit, was calculated by eq. 4 [22]:

$$CE = \frac{nFC_{H_2O_2}V}{\int_0^t I dt} \times 100\% \quad (4)$$

Where n is the number of electrons transferred for oxygen reduction to H₂O₂, F is the Faraday constant (96 486 C mol⁻¹), $C_{H_2O_2}$ is the concentration of H₂O₂ (mol L⁻¹), V is the bulk volume (L), I is the current (A), and t is the time (s).

2.4. Degradation of *p*-Np in EF system

The EF process was carried out in the same apparatus under similar operational parameters above, except the solution composition. The initial concentration of *p*-Np was 50 mg L⁻¹, and still, 0.05 M Na₂SO₄ was added as the supporting electrolyte. The pH was adjusted to 3 by concentrated H₂SO₄, which was regarded as the optimum value in EF system. In addition, 0.2 mM Fe³⁺ (ferric nitrate) was used as the catalyst instead of Fe²⁺ due to the cathodic electro-regeneration of Fe²⁺ [11]. The concentration of *p*-Np samples taken at an interval of 20 min was detected by high performance liquid chromatograph (HPLC, FL2200) with UV detector wavelength at 318 nm. The mobile phase was composed of chromatographically pure methanol and 0.1% H₃PO₄ (v/v) at 40/60. The separation was performed at 35 °C using a TMAQ-18 column ($\phi 4.6$ mm × 250 mm, 5 μ m) at a flow rate of 1.0 mL min⁻¹. The total organic carbon (TOC) of the samples was determined by a TOC analyzer (Analytikjena multi N/C 3100).

3. Results and Discussion

3.1. Morphology and properties of the cathode

Fig. 1a-c show the SEM images of samples CF, CF-A and CF-B, respectively. It was observed that the graphite felt was composed of an entangled network of carbon microfilaments with diameters around 15 μ m, which owned large specific surface areas. After chemical modification with absolute ethanol, many nanoscale particles and clusters, with an average diameter of 500 nm, appeared on the surface of the fibers (Fig. 1b and 1c). Since there was no involvement of other substances during preparation, the deposition

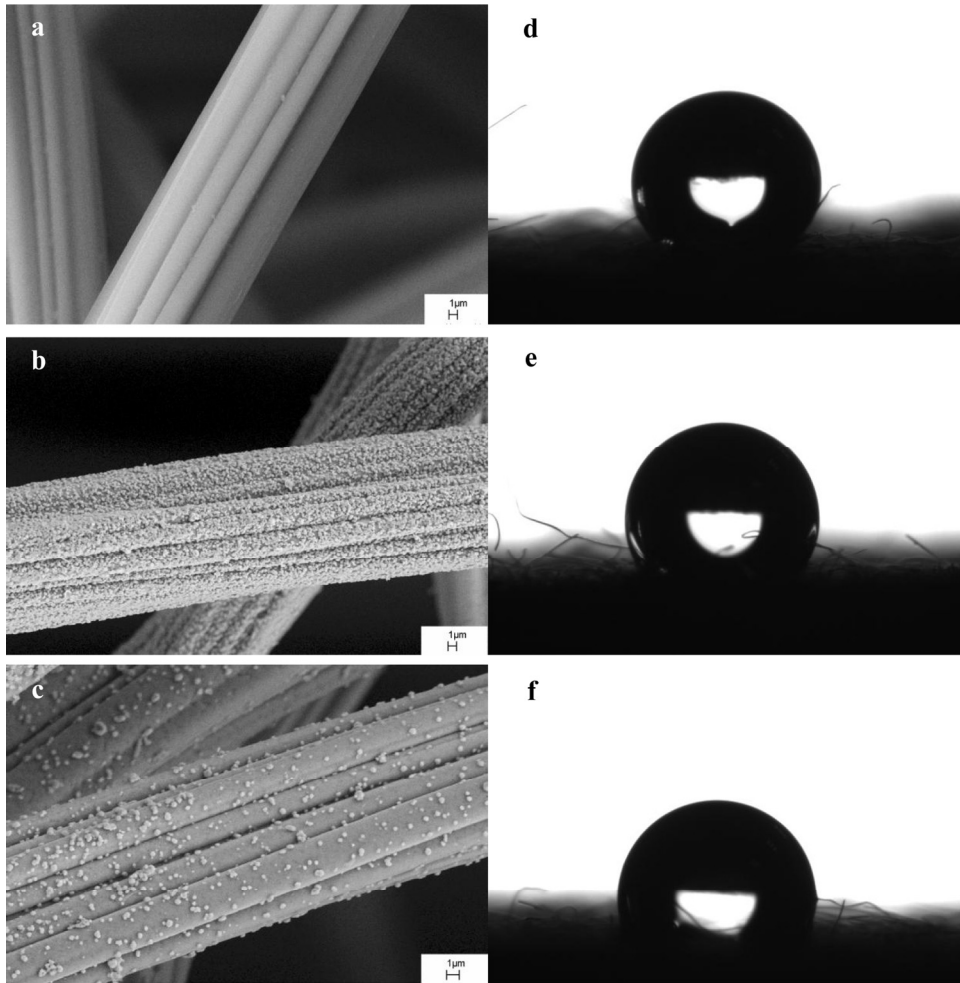


Fig. 1. SEM images and contact angles of CF (a, d), CF-A (b, e) and CF-B (c, f).

could mostly be composed of carbon, which was confirmed by the following Raman and XPS studies. The transformation from ethanol to carbon nanoparticles mostly occurred during the heating process ($150\text{ }^{\circ}\text{C}$), and the filament-wound structure of the graphite felts rendered the ethanol vapor to be kept within the samples, which made it possible for the nanoparticles forming or depositing on the fiber surface. It was also noticed that the deposition on the surface of CF-B was far less than that of CF-A, which might be induced by the presence of hydrazine hydrate, suggesting a possibility for controllable deposition process of carbon nanoparticles on the supports. The deposits can increase the gas-liquid contact interface in the modified samples, which is considered as one of the contributions to improve the catalytic performance.

In addition, Fig. 1d-f shows the contact angles of the sample CF, CF-A and CF-B, respectively. The better surface hydrophilic property of the modified samples was obtained, and the contact angles of CF, CF-A and CF-B were 141° , 123° and 110° , respectively. The results showed that the addition of hydrazine hydrate could weaken the hydrophobic property of the graphite felt more effectively as compared with absolute ethanol. The balance between hydrophobicity and hydrophilicity is very crucial to H_2O_2 production, especially for cathode without gas diffusion layer, because the dissolved oxygen needs to diffuse along with the electrolyte to the cathode surface, even the active sites [23]. For highly hydrophobic graphite felt, the improved hydrophilic surfaces could promote the electron transport and the mass transfer between the cathode and electrolyte, resulting in the improvement of the electrochemical performance.

3.2. Raman analysis

Fig. 2 shows the representative Raman spectra of CF, CF-A and CF-B, and each sample exhibits remarkable characteristic peaks for carbonaceous material. For CF, the peak at around 1350 cm^{-1} corresponding to the D band was attributed to vibrations of carbon

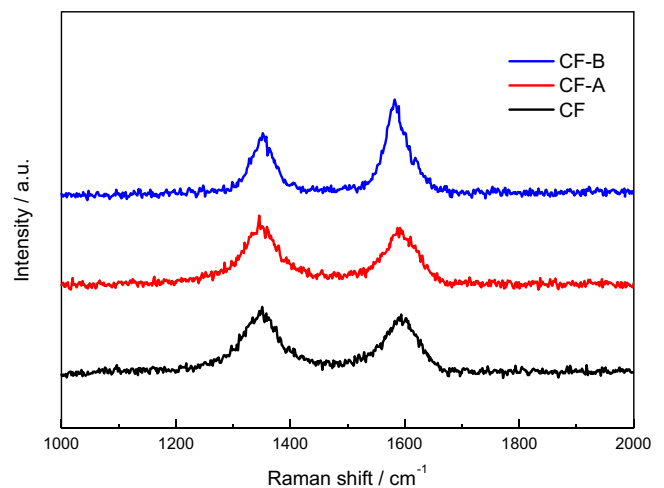


Fig. 2. Raman spectra of CF, CF-A and CF-B.

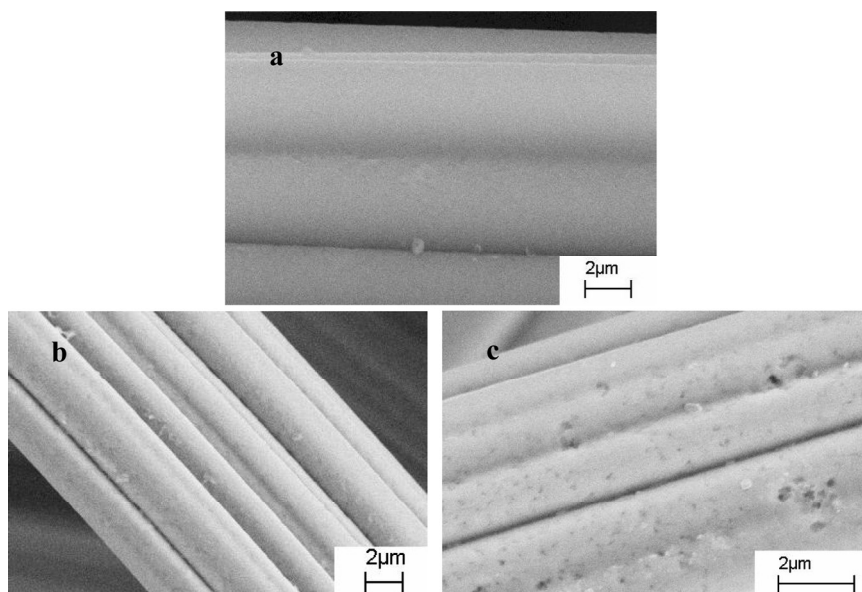


Fig. 3. SEM images of (a) CF, (b) CF-A and (c) CF-B only after refluxing treatment. Before analysis, CF-A and CF-B were rinsed in deionized water and then dried in air.

atoms with dangling bonds in plane terminations, which was typical for disordered graphite, and another peak at around 1595 cm^{-1} corresponding to the G band was ascribed to an E_g vibration mode of sp^2 -bonded carbon atoms in a 2D hexagonal lattice [24]. For CF-A, no shift occurred for the D and G bands as compared with CF, while for CF-B, the G band shifted down to around 1580 cm^{-1} , which could be due to the nitrogen doping introduced by hydrazine hydrate [25]. The intensity ratio between the D band and G band (I_D/I_G) of CF-A was 1.05, which was similar with CF ($I_D/I_G = 1.07$), suggesting that modification in absolute ethanol system had little influence on the integral graphitic degree of the material surface. However, a remarkable decrease of I_D/I_G value (about 0.65) was found in CF-B, indicating that the presence of hydrazine hydrate was favorable to improve the graphitic degree of the sample surface, which could promote the electron transportation in the cathode.

3.3. XPS analysis

The surface elements and functional groups of graphite felts before and after modification were studied by XPS analysis. The elemental compositions are listed in Table 1, and it can be seen that not only C and O elements but also Si element were observed in all the samples. The Si element could come from the material itself or the contaminations of instrument oil and glassware, since there was little change in Si element content before and after modification, it was barely considered as the major factor influencing the electrochemical performance of the samples. N element was only detected in CF-B due to the addition of hydrazine hydrate during modification. Since the data in Table 1 was collected over several regions of the electrodes, it suggested that the modification was effective and well-proportioned. It was also observed that the values of the

Table 1
The elemental compositions of CF, CF-A and CF-B.

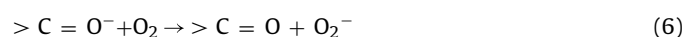
Sample	Concentration (at.%)			
	Carbon (C1s)	Oxygen (O1s)	Nitrogen (N1s)	Silicon (Si2p3)
CF	91.70 ± 0.74	7.46 ± 0.54	ND ^a	0.84 ± 0.10
CF-A	93.18 ± 0.94	6.01 ± 0.91	ND ^a	0.81 ± 0.04
CF-B	86.59 ± 0.47	11.98 ± 0.60	0.56 ± 0.05	0.87 ± 0.12

^a not detected

ratio between O and C (O/C) changed in different samples. For CF, the O/C was 0.081, which slightly decreased to 0.064 in CF-A due to the increase of carbon content by the deposition of carbon nanoparticles on the surface, while obviously increased to 0.138 in CF-B. It can be seen from Fig. 3 that the etching and corroding behaviors of hydrazine hydrate occurred on the surface of carbon materials after refluxing treatment, since the basal planes of the graphite can be attacked by molecular oxygen only at their periphery or at defect sites such as edge planes and vacancies [26], it might contribute to the increase of the O/C by inducing more oxygen-containing functional groups formation on the etched surface during heating in air.

Surface nitrogen-containing groups in CF-B were identified by deconvolution of the high-resolution XPS spectrum of N1s region (see Fig. 4a). The maximum peak centered at 401.1 eV was assigned to quaternary nitrogen, which was known as the 'graphitic nitrogen' species [27,28]. The weaker peaks centered at 398.4 eV and 404.8 eV could be attributed to pyridinic nitrogen and different N-oxide species, respectively [16,29,30]. The lone electron pairs of nitrogen atoms could form a delocalized conjugated system with the sp^2 -hybridized carbon frameworks, which resulted in a great improvement of electrocatalytic performance toward the ORR [20,28].

Fig. 4b shows the C1s spectrums of samples CF, CF-A and CF-B. For CF, the curve-fitting of C1s spectrum displayed three binding energy (BE) peaks corresponding to sp^2 carbons ($-C=C-$, $-C-C-$ or $-C-H$, BE = 284.6 eV), carbon coordinated to a single oxygen in hydroxyl groups or ethers ($-C-OH$, $-C-O-R$, BE = 286.2 eV), and carboxyl or ester groups ($-COOH$ or $-COOR$, BE = 289.2 eV) [16,31]. Compared to CF, the binding energy of the second peak corresponding to the groups such as $-C-OH$ or $-C-O-R$ in CF-A and CF-B decreased to 285.8 eV, which indicated that more hydroxyl groups instead of ethers existed on the surface of cathodes after modification, inducing an improved hydrophilicity. The other shoulder peak of CF-B at 287.2 eV was attributed to carbonyl, quinone groups or carbon-nitrogen single bond ($>C=O$, $-C-N$) [16,32], and the surface quinone species could behave as surface active sites to promote the H_2O_2 electro-generation as follow [18,33]:



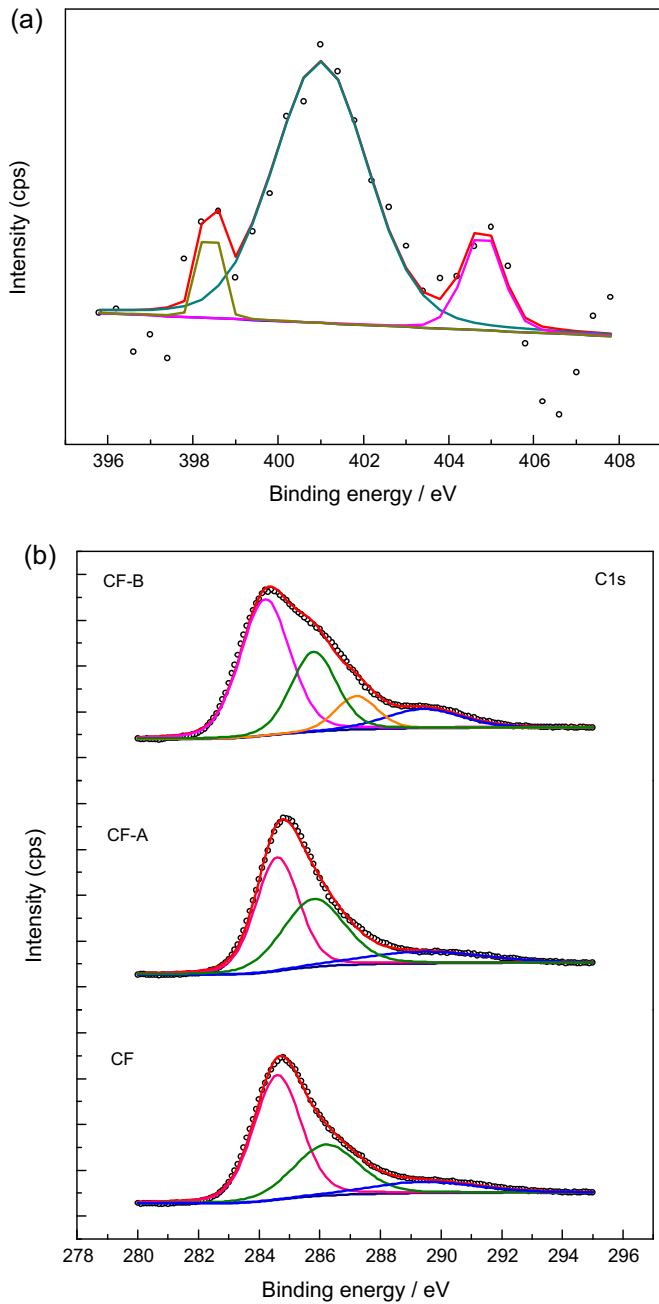
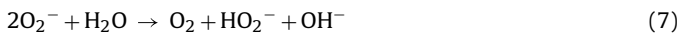


Fig. 4. The high-resolution XPS spectrum of (a) N 1s region and (b) C 1s region for the samples CF, CF-A and CF-B.



The surface oxygen in the form of acidic functional groups (i.e. -COOH, -COH, -COO-, R-OH, >C=O) can provide hydrophilic property to the modified surface to yield readily accessible dissolved oxygen, and it can also behave as surface-active sites favorable to accelerate electrochemical reactions [17]. Besides, the dominant peak in CF-B was shifted to a lower binding energy of 284.2 eV, indicating a more orderly graphitic structure, which could also be confirmed by Raman study.

Based on the forementioned characterization results, a possible chemical modification process can be illustrated in Fig. 5. Two processing stages refluxing and heating were carried out successively. The surface of the graphite felt maintained integrity after

refluxing treatment in the absolute ethanol condition, but were corroded and etched in the mixture solution of ethanol and hydrazine hydrate (Fig. 3). The degree of graphitization for the samples was barely changed in this processing stage (Fig. 2). For CF-A, the reagent liquid film adsorbed on the fibers might undergo a hydrothermal carbonization-like reaction to form carbon nano-particles with stronger hydrophilicity on the surface during the heating process. For CF-B, hydrazine hydrate introduced the nitrogen doping and restrained the carbonization to some extent, and then the oxidation occurred at the etched surface to increase the oxygen-containing functional groups during the heating process (Fig. 4). The higher graphitic degree and O/C in CF-B indicated a partial reconstruction of the surface structures.

3.4. Electrocatalytic performance

To investigate the effects of such a chemical modification on electrocatalytic activity of cathodes toward ORR, cyclic voltammetry was carried out on CF, CF-A and CF-B, as shown in Fig. 6. It could be seen that standard voltammograms with total irreversibility were obtained for all samples, and the modified cathodes exhibited stronger current responses for ORR and more negative hydrogen evolution potentials than the original one. It can be seen from eqs. 1 and 9 that the ORR was a proton-consuming process, which could compete with the H₂ evolution reaction at the cathode, as a result, the improved ORR process after modification, especially for those occurred at the less negative potentials, could effectively inhibit the H₂ production. In addition, the ORR tended to be triggered at less negative potentials after modification, which indicated a much faster electron transfer kinetics for ORR on the modified cathodes [28]. For CF, there was a single broad peak with potential range from -0.3 to -0.8 V, mainly attributed to the H₂O₂ production reaction (eq. 1). Whereas for CF-A and CF-B, two obvious oxygen reduction peaks at around -0.45 V, -1.3 V and -0.55 V, -1.0 V were observed, corresponding to the two-electron transfer process towards ORR (i.e. H₂O₂ electrochemical generation, eq. 1) and also the higher number electron transfer processes for oxygen molecule (e.g. H₂O electrochemical generation, eq. 9), successively [4,10].



Compared to CF-A, the current density of CF-B was much higher, which indicated that CF-B had a better electrocatalytic activity for oxygen reduction than CF-A. These results can be explained from the change of the surface chemistry after different chemical modification by XPS and Raman analysis above.

To further investigate the effects of chemical modification on electrocatalytic activity of H₂O₂ production, the experiments were performed at a constant potential of -0.65 V vs. SCE in order to avoid the other competitive ORR processes at cathodes as much as possible. Fig. 7 shows the concentration and current efficiencies of H₂O₂ electrochemical generation on different cathodes. The accumulations of H₂O₂ at CF, CF-A and CF-B after 120 min were 67.5, 109.8 and 175.8 mg/L, respectively. The increased yields of H₂O₂ for CF-A and CF-B could be induced by the increased current responses for ORR after modification, which indicated the positive effects of chemical modification on H₂O₂ production under the given conditions. The current efficiencies of CF, CF-A and CF-B, as shown in the insert Fig. 7, were 89.7%, 84.9% and 80.8%, respectively, indicating a decline in current efficiency after modification. It was observed from cyclic voltammetry that the chemical modification not only encouraged the two-electron transfer process for H₂O₂ electrochemical generation but also promoted the side reaction of H₂O₂ decomposition (eq. 10), resulting in a drop of current efficiency for the modified electrodes CF-A and CF-B. In addition, the increased current responses in the modified systems simultaneously promoted the parasitic reactions at anode (eqs. 11 and

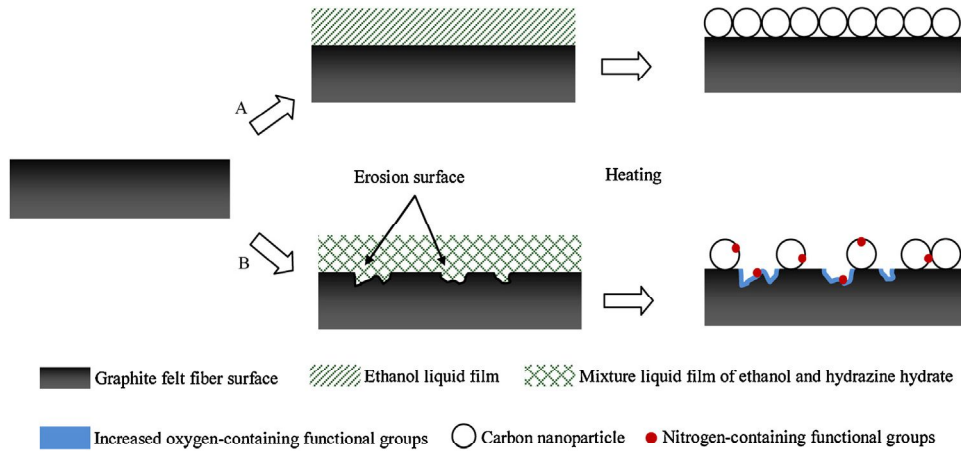


Fig. 5. Illustration of the chemical modification on graphite felt.

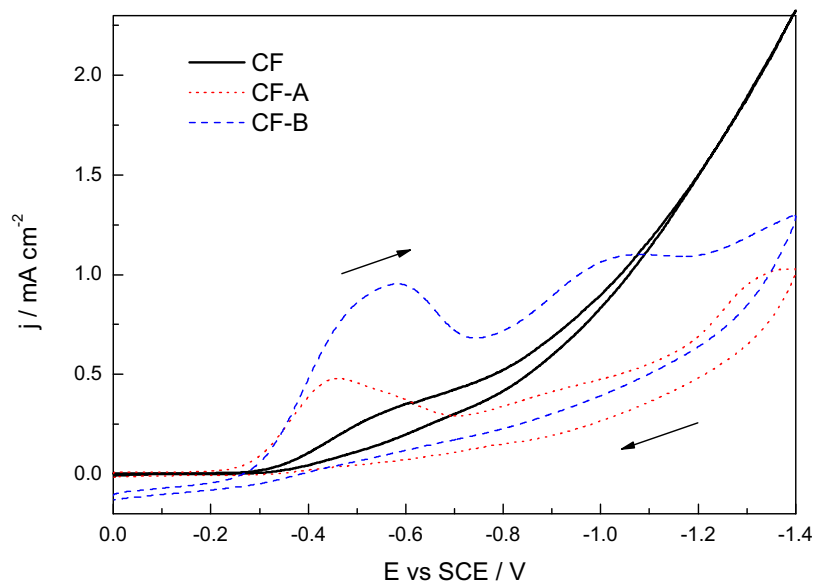


Fig. 6. Cyclic voltammograms of CF, CF-A and CF-B.

Conditions: Scanning potential range 0 ~ -1.4 V, 0.05 M Na₂SO₄, O₂ saturated.

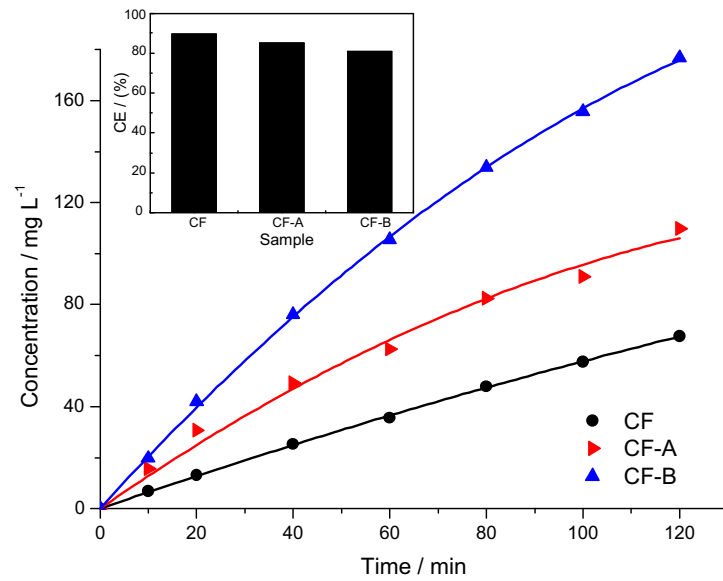


Fig. 7. The concentration and current efficiencies of the H₂O₂ electrogeneration at different cathodes. Conditions: E = -0.65 V, 0.05 M Na₂SO₄, O₂ flow rate 0.4 L min⁻¹.

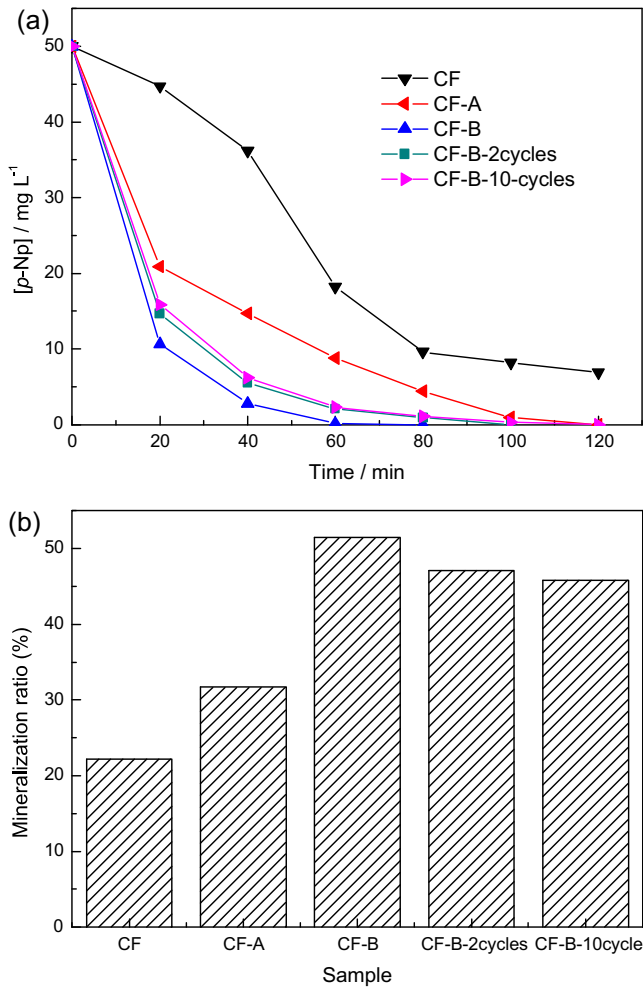


Fig. 8. (a) The evolution and (b) mineralization ratios of *p*-Np at CF, CF-A, CF-B, and CF-B used for 2 and 10 cycles. Conditions: $E = -0.65$ V, 50 mg L^{-1} *p*-Np, $0.05 \text{ M Na}_2\text{SO}_4$, 0.2 mM Fe^{3+} , $\text{pH} = 3$, O_2 flow rate 0.4 L min^{-1} .

12) in an undivided cell, especially for CF-B, which also induced a decrease of the current efficiency [34].



The electrocatalytic performance of the CF, CF-A and CF-B in EF system was evaluated by the degradation of *p*-Np in Fig. 8. It can be seen that the electrocatalytic activity increased after chemical modification. For CF, CF-A and CF-B, the degradation efficiencies of *p*-Np were 6.6%, 58.3% and 78.7% after 20 min, respectively. The remarkable improvement in the initial stage might be encouraged by the increased current responses which could promote the production of H_2O_2 and the reduction of ferric ions, increasing the amount of $\cdot\text{OH}$, as is shown in Fig. 9. The tendency of mineralization ratios in Figure 8b was consistent with the evolution of *p*-Np in Fig. 8a, and the TOC removal ratios were 22.2%, 31.7 and 51.4% for CF, CF-A and CF-B, respectively. These results showed that the modified cathodes could efficiently promote the degradation efficiency of the pollutants as compared with the unmodified one. The CF-B possessed the highest electrocatalytic activity in EF system, which could be ascribed to the remarkable advantage of the surface structures and properties after modification as mentioned above. Since the stability of electrodes is important for their practical application, the used

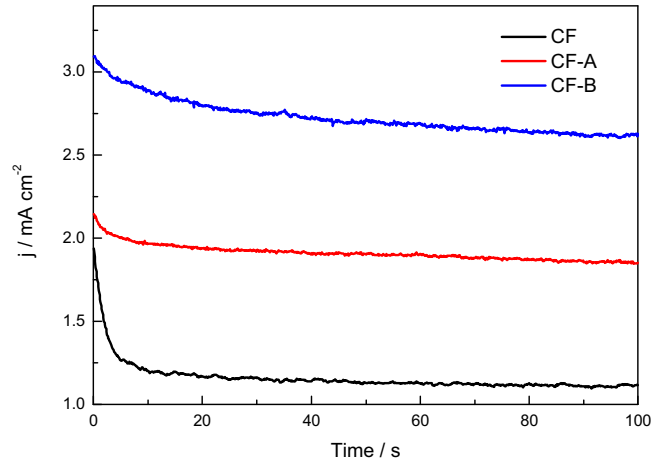


Fig. 9. Current-time curves of the CF, CF-A and CF-B.

CF-B cathode was cleaned with deionized water and then reused for degradation of *p*-Np under the same conditions. It could be seen from Fig. 8 that there was a slight decrease in degradation of *p*-Np when the second use of CF-B, but after that the decontamination ability of recycling cathode reached the steady state, and the mineralization ratio after 10 cycles was still above 45%, indicating that the modified electrodes was stable and reusable.

4. Conclusions

We reported a simple method to modify graphite felt using low-cost chemical reagents ethanol and hydrazine hydrate to increase their electrocatalytic performance in electro-Fenton system. Carbon nanoparticles were formed on the surface of the microfilaments after ethanol modification. Oxygen and nitrogen-containing functional groups obviously increased in the presence of hydrazine hydrate. The stronger hydrophilicity and faster electron transportation were obtained in modified samples, which could efficiently improve the electrocatalytic activity for ORR process. The modified electrodes resulted in obviously increased H_2O_2 accumulation and enhanced *p*-Np degradation efficiency in EF system as compared with the unmodified one. And the modified electrodes were stable and reusable, indicating that the reported chemical modification is a promising cathode modification alternative to improve the efficiency for EF system.

Acknowledgements

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