

Review

Research and Application Progress of Modified Graphite Felt Gas Diffusion Cathode in Organic Wastewater Degradation

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Abstract

Modified graphite felt is a widely studied cathode material at present. Because of its corrosion resistance, high specific surface area and low cost, it shows great potential in electrochemical oxidation reduction. In this paper, various modification methods of graphite felt, such as introduction of oxygen-containing functional groups, doping of hetero-atoms, deposition of carbon materials, hydrophobicity and so on, are reviewed, in addition, the application effect of modified graphite felt in the removal of organic pollutants in water environment was summarized. Finally, the future research hotspots and challenges were prospected.

Keywords: hydrogen peroxide, oxygen reduction reaction, graphite felt, fenton reaction, degradation of organic pollutants

Introduction

Water is one of the most important resources for human survival. In recent years, the presence of organic pollutants in rivers, lakes and drinking water caused by industrial and agricultural waste has caused serious pollution of the aquatic environment, as well as having an impact on human health because of their high toxicity and danger. In particular, wastewater containing pesticides, pharmaceuticals and dye are characterised

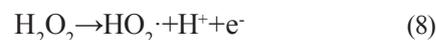
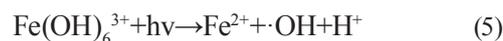
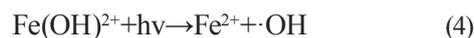
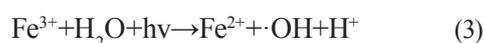
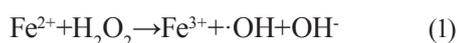
by high emissions, varying nature, difficult degradation and high toxicity [1-5]. Therefore, effective methods are needed to effectively remove the refractory organic pollutants in wastewater, such as biological method [6, 7], physical method [8, 9], chemical method [10] and electrochemical method [11-13]. Among them, the electrochemical method to remove the refractory organic pollutants in wastewater removal has a broad application prospects.

Advanced oxidation process (AOP) is a technology of wastewater treatment, in which electrochemical advanced oxidation (EAOP) has the advantages of good environmental compatibility, green process, less secondary pollution, simple operation and high safety

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[14]. There are two main oxidation pathways in EAOP, one is direct oxidation, in which pollutants are directly attached to the anode surface to react and degrade to non-toxic or low toxic substances, the other is indirect oxidation, hydroxyl radical ($\cdot\text{OH}$) is a kind of strong oxidant, which can oxidize pollutants, and $\cdot\text{OH}$ has the characteristics of strong oxidation, short life, high treatment efficiency and no secondary pollution [15, 16]. EAOP is a common and effective method to remove pollutants from wastewater by the $\cdot\text{OH}$ produced in electro-Fenton (EF) and electro-optical Fenton (SEF) processes (Eqs 1-6) [17-20].

Electrode material is the key factor to determine EAOP, the anode degrades organic pollutants mainly through electron transfer and $\cdot\text{OH}$ oxidation, the common anode materials are titanium, platinum, carbon such as boron-doped diamond (BDD) electrodes, and metal oxide electrodes such as lead dioxide (PbO_2) and tin dioxide (SnO_2) [21]. The cathodic reaction mechanism (shown in Fig. 1) uses either dissolved or anodic oxygen to produce hydrogen peroxide (H_2O_2) by oxygen reduction (ORR) with two electrons (Eq. 7), the formation of $\cdot\text{OH}$ (Eqs 8-9) from the generated H_2O_2 can lead to the mineralization of the organic pollutants to H_2O and CO_2 . Therefore, the effect of cathode material on the amount of H_2O_2 production will also determine the effect of organic mineralization [22]. Carbon-based cathodes have many advantages, such as wide source, low price, good stability and conductivity, which make them important materials for producing H_2O_2 [23], such as graphite [24], carbon nanotubes [25], graphene [26, 27] and activated carbon fibers [28, 29], and graphite felt [30, 31]. Second, the operating parameters have great influence on the production of H_2O_2 and the degradation of organic pollutants by EAOP, including pH, current density, initial concentration of organic compounds, temperature, air/ O_2 flow rate and so on [32].



Among carbon-based cathodes, graphite felt (GF) is a typical electrode with three-dimensional structure, which has the advantages of easy access, high specific surface area, strong corrosion resistance, etc. In addition, the material has good chemical stability, easy processing and low cost [33]. In recent years, many research hotspots focus on GF as the cathode to reduce oxygen to produce H_2O_2 , and then apply it to the degradation of organic pollutants in water, but the H_2O_2 production rate of GF is relatively low. Therefore, effectively improving the production of H_2O_2 is the focus of current research. At present, various modification methods of GF cathode are often studied to solve the shortcomings of slow GF reactivity and low ORR selectivity [34]. Find all publications and all years of publication in the database. The main modification methods of GF include (1) With oxidation modification and activation of electrodes as keywords, introducing oxygen-containing functional groups (OGs) to improve the hydrophilicity of carbon materials. OGs can also be used as the active site of the reaction. Therefore, the introduction of OGs is expected to improve the electrocatalytic activity of carbon materials. (2) Using different atom doping and co-doping on GF surface as key words, metal/non-metal doping can regulate the electronic structure and improve the selectivity and activity of H_2O_2 synthesis. (3) The deposition of high performance carbon materials increases the specific surface area and active sites, using high performance carbon materials and GF as keywords. Deposition of high performance carbon materials leads to enhanced

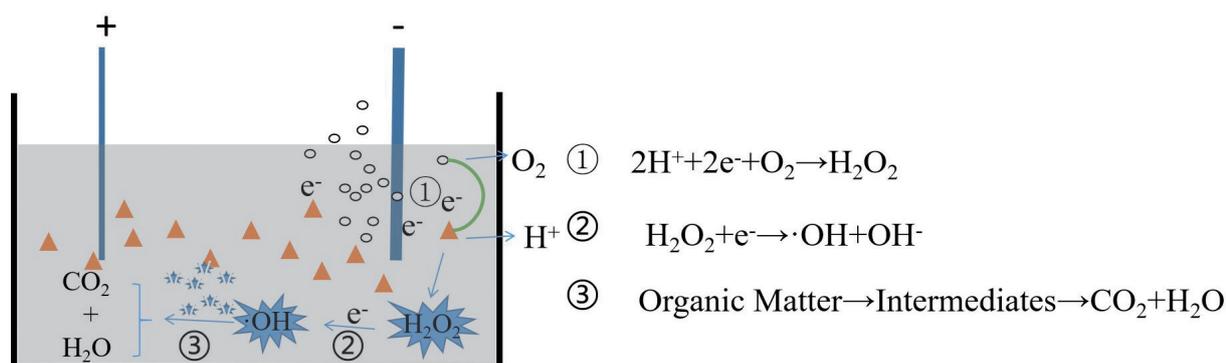


Fig. 1. Schematic diagram of the cathodic reaction mechanism.

2-electron ORR. (4) Increasing the gas-liquid-solid three-phase interface improves O_2 transfer, with wettability as the keyword, changing the wettability of the graphite felt surface.

Results and Discussion

Introduction of Oxygen-Containing Functional Groups

When OGs are introduced on the electrode surface, common functional groups include hydroxyl group (-COH), ether bond (-C-O-R), carbonyl group (-C=O), carboxyl group (-COOH), ester group (-COO) and adsorbed molecular water (-H-O-H), these OGs are characterized by high specific surface area, hydrophilicity, sufficient active sites and enhanced conductivity. The modified method is simple and has low cost [35]. The method of introducing OGs into electrode surface can be divided into chemical oxidation and electrochemical oxidation. Chemical oxidation such as KOH activation, water activation, HNO_3 , H_2O_2 and so on are used to modify carbon materials. Electrochemistry is modified without the use of oxidants by adjusting the current and treatment time, and the method is more environmentally friendly and economical [36]. The introduction of different functional groups, keyed to oxidation modification and activation of the electrode, improves the electrode hydrophilicity, pore structure and active sites in order to produce more H_2O_2 and a more efficient way of pollutant removal.

The introduction of oxygen-containing functional groups modified GF is mainly to study the effects of oxygen and oxygen-containing functional group's types on electrocatalytic activity of electrodes. Table 1 summarizes the elemental composition and proportion of oxygen-containing functional groups in GF after modification. Lu et al. [37] introduced different oxygen-containing groups in different positions of carbon materials, including -COOH, C=O, C-OH and -COO, and the catalytic activity may only be affected by some highly active functional groups. The study found that the activity and selectivity of ORR to generate H_2O_2 are related to oxygen content. Wang et al. [38] used Fenton reagent, H_2O_2 reagent and electrochemical oxidation respectively to modify GF to observe the changes of oxygen-containing functional groups on the surface. Through X-ray photoelectron spectroscopy (XPS) analysis, they found that the main functional group increased on the surface of carbon materials was -COOH. After electrochemical oxidation, the content of -COOH in the sample increased from 1.73% to 68.25%, and studies showed that the increased -COOH could provide the active site, and the provision of electrode activity was related to the increase of the content of -COOH functional groups.

Chemical Oxidation

Chemical oxidation requires the introduction of oxygen-containing functional groups under the conditions of concentrated acid and alkali, such as KOH activation, acetic acid activation, CO_2 activation, etc. to improve the mass transfer rate of O_2 on the electrode surface by changing the physicochemical properties and catalytic performance of the graphite felt surface, so as to improve the electrocatalytic performance. Studies show that the introduction of oxygen-containing functional groups on the surface of the material increases the hydrophilic energy of the material, improves the catalytic activity and conductivity of the electrode material, and effectively improves the production of H_2O_2 . Table 2 summarizes the conditions for the introduction of oxygen-containing functional groups to modify GF, the production of H_2O_2 and the degradation of pollutants. It has been found that in CO_2 modified carbon fiber, the specific volume of carbon fiber increases with the increase of CO_2 temperature, and at the same time, micropores are generated on the carbon material [44]. Therefore, Chang et al. [41] treated GF under high temperature CO_2 atmosphere and observed rougher surface and more pores through scanning electron microscopy (SEM), which proved that the surface area of CO_2 -ACT-GF increased and it had more oxygen-containing groups (C-OH, C=O and H-O-H) under CO_2 activation. At the same time, the hydrophilicity of CO_2 -act-GF surface is increased, which is more conducive to the electrochemical reaction. Pan et al. [40] obtained AGF1100 by acetic acid activation at high temperature, and observed uniform porous structures under SEM. These structures can be used as active sites to improve ORR, and the activation can cause the increase of C=O, C-OH and O=C-O, thus effectively improving the catalytic activity. Under the condition of -0.7 V, the H_2O_2 yield within 1 hour is 472.9 mg/L, which is much higher than that of GF before modification, indicating that the existence of porous structure improves the diffusion of reactants and products in the electrode. The electrode can completely degrade Rhodamine B within 15 min in the electro-Fenton (EF) process, and the kinetic constant is twice that of GF before modification. After activating GF by KOH at high temperature, Wang et al. [39] observed by SEM that the surface of GF became rough and had grooves, which increased the specific surface area of the electrode and thus increased the active surface area, therefore, the ORR reaction can be improved. The degradation efficiency of the electrode in dimethyl phthalate (DMP) was 10 times that of GF before treatment. Qi et al. [45] used $(NH_4)_2S_2O_8$ as modifier to modify GF by hydrothermal method. Compared with other modification methods, this method is simple and low cost, and can be used in large-scale production. The amount of H_2O_2 produced by the modified H-GF was 3.06 times as much as that of the original GF

Table 1. The composition and proportion of various oxygen-containing functional groups in different modified electrodes.

Samples	Oxygen-containing groups					Ref.
	C-OH (%)	C=O (%)	H-O-H (%)	O=C-O (%)	O/C	
AGF-900	8.26	4	1.95	-	0.17	[39]
AGF1100	65.16		-	4.82	0.07	[40]
CO ₂ -act-GF	39.5	28.1	9.11	-	0.44	[41]
CF-15	35.44	33.57	-	0.084	0.36	[42]
B-CNT/TA-GF	-	39.2	11.8	-	-	[43]
GF-E-10	9.46	28.02	13.84	-	0.324	[38]
GF-F-20	11.85	32.89	47.33	-	0.105	[38]

Table 2. H₂O₂ production and pollutant removal rate of GF modified with oxygen-containing functional groups.

Samples	Modification conditions	H ₂ O ₂ (mg/L)	Time (min)	C ₀ (mg/L)	Degradation efficiency (%)	Ref.
AGF-900	GF is immersed in KOH aqueous solution until KOH crystal is separated and heated in tube furnace, then washed and dried.	79.2	120	50	100	[39]
AGF1100	The acetic acid flow obtained from the liquid gasification unit was injected into the gas path system and kept for 1 h after annealing at 1100°C in N ₂ atmosphere. Cool to room temperature before drying in the oven.	472.9	60	5	100	[40]
H-GF	RGF was impregnated with 0.25 M ammonium persulfate solution and treated with ultrasonic wave. The ammonium persulfate solution containing GF was heated in an autoclave at 180°C. Leave in the oven for 24 h.	20.54	40	20	100	[45]
CF-5	0.05 M aqueous solution of Na ₂ SO ₄ was used as supporting electrolyte. The potential of the working electrode was scanned back and forth between 0 V and 2 V for 5 cycles.	239	120	50	78(TOC)	[42]
GF-9	The pre-treated GF was immersed in a hydrothermal synthesis reactor containing concentrated HNO ₃ , heated at 90°C, and then dried.	17.52	120	80	55.64(TOC)	[48]
GF-I-3	Modified at 50 mM Na ₂ SO ₄ , -1.2 V vs. Ag/AgCl, 200 mA for 30 min	46.8	50	1 mM	-	[49]
GF-30	0.4 L/min O ₂ , pH 3, -0.60 V (vs. SCE), 0.2 M NH ₄ HCO ₃ aqueous solution	163.3	120	-	-	[46]
CF-HA-10%	It was soaked in a mixture of 100 mL ethanol and 10% hydrazine hydrate and annealed at 150°C for 2 h after reflux at 60°C.	176.8	120	50	100	[50]
GF-5	100 mA and 25°C for 5 min, PH = 7, O ₂ flow rate 0.4, -0.65 V (vs. Ag/AgCl)	30.4	60	30	79.5(TOC)	[51]
GF-C	The electrolyte was H ₂ SO ₄ aqueous solution, the current density was 90 mA/cm ² , and the treatment time was 25 minutes	110.5	120	60	88.7(TOC)	[52]

in 40 minutes. The reason for the substantial increase of H₂O₂ may be the increase of oxygen-containing groups and active sites. After the oxidative degradation of diuretics in EF process, its biological toxicity is also effectively reduced.

Electrochemical Oxidation

Chemical oxidation is the modification of oxygen-containing functional groups without the use of oxidants. Under the action of an electric field, the

oxidizing ions in the electrolyte move to the GF and oxidize to form oxygen-containing functional groups. Such as anodic oxidation [46], cyclic voltammetry [36] and so on. Compared with chemical method, this method is more economical and environmental friendly, and its controllability and practicability also make this method more promising. Compared with GF before modification, the oxygen-containing functional groups C-O, C=O, COOH and C-OH were significantly increased. Zhou et al. [42] studied the modification of GF by anodic oxidation to improve its electrocatalytic activity. -COOH, C-OH, C=O were detected on GF after anodic oxidation, and the electrocatalytic activity of ORR after modification was much higher than that of the original electrode, at the same time, the production of H_2O_2 was 2.7 times higher than before, and after 20 cycles, it still showed a stable effect on P-Nitrophenol. Miao et al. [47] cyclically polarized the GF electrode at a rate of 10 mV/s in 0-2 V in 10% H_2SO_4 solution, and XPS observed that more oxygen-containing functional groups (-COOH, C=O) were introduced to the electrode surface, the H_2O_2 production of GF-10 in 20 min was 6 times that of untreated GF.

Doping with Hetero-Atoms

By doping N, F and other nonmetallic atoms, the structure of carbon materials is rearranged, and the active sites and ORR selectivity of carbon materials are increased. In heteroatom-doped carbon materials, the electrocatalytic activity of carbon materials is increased by regulating the connection of a large number of conjugated sp^2 - sp^2 and destroying the integrity of π

system. Hetero-atom doping can change the electronic structure of carbon materials and generate local positive and negative charge groups without affecting the conductivity. For example, some negatively charged atoms become active sites by polarizing the surrounding carbon atoms to become positively charged [53]. Heteroatom doping alters the electronic and surface structure of GF, with different atomic doping and co-doping on the GF surface as the key to forming active sites as well as improving pore size and enhancing electrode electrocatalytic performance. In Table 3, the conditions of GF modified by heteroatom doping, H_2O_2 production and pollutant degradation were summarized.

N-doped

Doping N atom is the most widely studied, because the radius of N atom is similar to that of C atom, which can easily replace C atom in carbon material. N atom has higher electronegativity than C atom. By adjusting the charge distribution of sp^2 , more structural defects will be generated and the electron transfer rate will be improved. Gong et al. [58] have studied that vertically aligned nitrogen-doped carbon nanotubes have obtained higher electrocatalytic activity and stability under alkaline conditions, and proved that nitrogen doping can be applied to the development of other metal-free high-efficiency ORR. Yu's group [59] studied different forms of N-doped carbon materials to improve H_2O_2 production and pollutant treatment. In this study, polyaniline (PANI) was introduced into GF by electrodeposition method. The content of N atom in GF increased from 2.94% to 17%, and N-atom doping was

Table 3. H_2O_2 production and pollutant removal rate of doping modified GF cathode.

Samples	Modification conditions	H_2O_2 (mg/L)	Time (min)	C_0 (mg/L)	Degradation efficiency (%)	Ref.
g-C ₃ N ₄ /GF	The load of g-C ₃ N ₄ was deposited by electrophoresis at a constant current density of 2 mA/cm ² for 20 minutes.	496.5	360	200	100	[20]
GF/CNB-1	The mass ratios of carbon powder, melamine, and boric acid was 1:0.1:0.05.	152.8	240	50	61	[54]
GF-Co	Carbon black and metal nitrate are mixed in an ultrasonic bath and then dried. An appropriate amount of metal, PTFE, distilled water, and n-butanol are mixed in an ultrasonic bath to form a highly dispersed mixture	554.8	120	50	82	[55]
GF-W-Mo	The cathode electrolyte was replaced by a mixture of Na ₂ WO ₄ ·2H ₂ O and Na ₂ Mo ₄ ·2H ₂ O. Calcination in air after electrodeposition.	-	-	20	33.7±2.7	[56]
Fe-Cu/HGF	Under ultrasonic treatment, HGF was immersed in PVP, Cu(NO ₃) ₂ and K ₃ [Fe(CN) ₆] solution, and after drying in the oven, the material was calcined for 1 h in N ₂ environment, and then let cool to room temperature.	-	-	20	100	[57]

realized and ORR was increased. The porous structures were observed on GF by SEM, which promoted the diffusion of O_2 on the surface. The linear sweep voltammetry (LSV) showed that modified GF had a higher response current. The results showed that the introduction of N atom further enhanced the reduction reaction of O_2 , improved the production and selectivity of H_2O_2 , and made more H_2O_2 form $\cdot OH$. When $pH = 3$, the removal rate of bisphenol A (BPA) from modified GF can reach 100% within 15 min. In another study, Yu et al. [60] used N-rich zeolitic imidazole framework-8 (ZIF-8) as a precursor and carbonized nitrogen-doped porous carbon (NPC) to prepare NPC/GF cathode. The modified electrode promoted electron transfer, improved ORR, and made the electrode have higher electrocatalytic activity. When $pH = 7$ and current density is 12.5 mA/cm^2 , H_2O_2 increases to 118.4 mg/L . Compared with the TOC removal rate of 15% before modification, the phenol removal rate of 100% and TOC removal rate of 82% after 200 min of NPC/GF cathode, and the difference of pollutant removal rate is reflected in the significant increase of H_2O_2 production by NPC/GF cathode.

F-doped

Due to the high electronegativity of F, the electronic structure of carbon is adjusted according to the mixing of F, which provides more active sites for ORR to produce H_2O_2 . Zhao group developed different F-containing precursors to enhance electrochemical redox production of H_2O_2 . Zhao et al [61] prepared aluminum-based MOF as precursor by hydrothermal method, and removed aluminum by hydrogen fluoride (HF) and H_2SO_4 washing to achieve F doping, the material has good surface area and H_2O_2 synthesis performance. At $pH = 1$, the generation rate of H_2O_2 was $112.6\text{-}792.6 \text{ mmol h}^{-1} \text{ g}^{-1}$ and the current efficiency was 81.6-93.6% at -0.1 to -0.6 V. The formation rate of H_2O_2 is related to the content of F. when the content of F exceeds a certain amount, the electron conductivity decreases and the production of H_2O_2 decreases due to the existence of a large number of defects, when the optimum F content is 3.41%, the optimum ORR can be obtained to produce H_2O_2 . In another study, charge polarization was induced by incorporation of F into carbon materials, which not only increased the production of H_2O_2 but also accelerated the cycling of Fe^{3+} and Fe^{2+} . In the treatment of atrazine, the removal rate of TOC reached 56% at 60 min, which was 33% higher than that before modification [62].

Metal Atomic Doping

Other heteroatom doping studies are less, some researchers doping metal atoms to improve ORR. Chen et al. [63] coated titanium (Ti) net on GF to form GF-Ti. Combined with electrolysis - ozone (O_3) - Gf-Ti, O_3 reduction in GF-Ti cathode accelerated the generation

of $\cdot OH$. In Cu (II) recovery, the recovery rate reached over 90% and the TOC removal rate reached over 80%. Studies have shown that this electrode can be used as an important method to remove heavy metal complexes in organic wastewater. Liang et al. [55] prepared a kind of GF cathode modified by transition metal cobalt Co. It was observed in the SEM image that after loading Co, a large number of interconnected particles appeared on the smooth GF fiber, which significantly changed the surface characteristics of the cathode. At $pH = 3$, the H_2O_2 production of GF-Co reached 554.8 mg/L , which was 15.5 times higher than that of pre-modified GF. In addition to the above several metal atoms, Adzic et al. [64] observed 2-electron reduction on the surface of gold (Au) and demonstrated that nanogold structures can serve as active catalysts. Noble metals, such as platinum (Pt) and palladium (Pd), are often used as efficient catalysts for the synthesis of H_2O_2 from ORR. Pt and Pt-based catalysts are recognized as the most advanced electrocatalysts. Doping Pt further improves the performance of cathode materials, such as common Pt atoms, Pt nanoclusters and so on. Huang et al. [65] loaded Pt onto carbon nanotubes by electrodeposition, and the activity of the modified electrode remained basically unchanged in the accelerated durability experiment, indicating that it has stronger durability and catalytic activity after Pt loading. The Pt nanoclusters catalysts studied by Zhou et al. [66] showed excellent electrocatalytic activity and high stability.

Multi-Atom Doping

Some researchers try to doped two or three kinds of atoms at the same time, hoping to obtain better performance than doped single atom carbon materials. Fe-Cu/HGF composite cathode was prepared by using low-cost copper (Cu) and iron (Fe). It was found that the response current of Fe-Cu/HGF was stronger than that of GF, and the reduction peak of Fe-Cu/HGF composite cathode was higher than that of GF, the cathode exhibited better hydrophilicity than that of the modified GF, with more defects and larger active surface area. The cathode can effectively remove diuron on the basis of reducing energy consumption [57]. Wang et al. [67] loaded Cu onto graphene oxide (GO) modified GF to prepare the Cu-Go-GF cathode. The X-ray energy spectrum (EDS) observed Cu, C and O, indicating that Cu and GO were successfully doped in GF, and the increase in the percentage of O atoms indicated the introduction of oxygen-containing functional groups, which could provide the active site. The removal rate of nitrate by Cu-GO-GF cathode is 92%, which is more than 50% higher than the removal rate of nitrate by GF, Cu-GF and Go-GF, indicating that the electrocatalytic activity of the prepared cathode is significantly improved. Ding et al. [54] developed a graphite felt cathode doped with N and B. The modification method increased the H_2O_2 from 9.39 to 152.8 mg/L ,

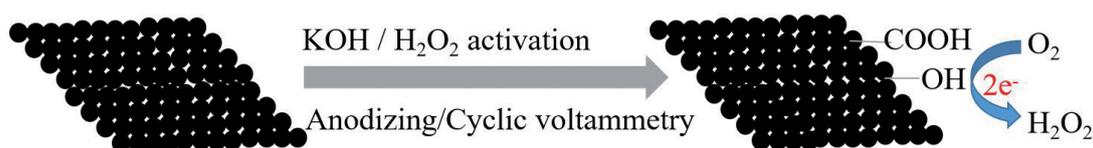


Fig. 2. Schematic diagram of ORR mechanism of introducing oxygen-containing functional group on GF.

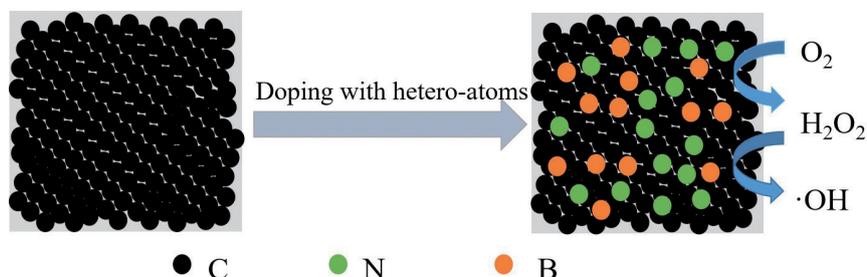


Fig. 3. Schematic diagram of ORR mechanism of B and N co-doped GF.

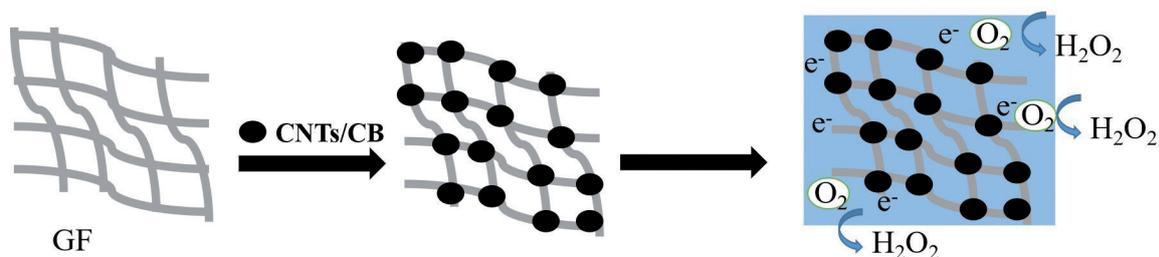


Fig. 4. ORR reaction diagram of carbon materials deposited by GF.

and the current efficiency increased to 70.3%. At the same time, EF and electrocoagulation system were used to completely degrade dibutyl phthalate (DMP), and the TOC removal rate reached 80% within 2 h. The synergistic effect of EF and electro-coagulation system is higher than that of EF process. As shown in Fig. 3, co-doped N and B increased ORR.

Deposition of Carbon Materials

As shown in Fig. 4, high performance carbon materials and GF as keywords, other high-performance carbon materials, such as carbon nanotubes (CNTs), graphene and carbon black (CB), were introduced into the carbon-based substrate to enhance the 2-electron ORR reaction to generate H_2O_2 . Table 4 summarizes the conditions of GF modified by carbon deposition materials, H_2O_2 production rate and pollutant degradation rate.

The results show that water leakage and electrolyte leakage can be reduced and O_2 transfer can be increased under the action of CB and PTFE. Yu et al. [68] studied the optimal ratio of CB and PTFE modified GF, the production of H_2O_2 under the modified condition and the treatment effect of methyl orange (MO) in EF. The results showed that when CB and PTFE

were deposited on GF surface according to the mass ratio of 1:5, the H_2O_2 production increased by about 10.7 times. When $\text{pH}=3$, it takes 30 min to decolorize methyl orange before modification in EF system, and the energy consumption for complete removal is 2.25 kWh/m^3 . After modification, it only takes 15 min to decolorize methyl orange, and the energy consumption decreases to 0.75 kWh/m^3 . These results show that, after modification, GF has better performance in degrading MO and consumes less energy. At the same time, Cai et al. [69] used this electrode to degrade 2, 4-dichlorophenoxyacetic acid (2,4-D). Under acidic conditions with a current density of 5 mA/cm^2 , the degradation rate of 2,4-D increased by 8 times. Due to the effective increase of H_2O_2 production, the current efficiency increased and the energy consumption decreased, and the contribution rate of $\cdot\text{OH}$ to the treatment of 2,4-D was 57.5%. This study showed that GF modified by CB and PTFE could be used as an efficient cathode for degradation of organic wastewater.

Graphene is a two-dimensional hexagonal honeycomb crystal consisting of a single layer of carbon, which has excellent optical properties, strength, hardness, electrical conductivity and high specific surface area [70]. Yang et al [71] developed a novel GF cathode modified by electrochemically exfoliated

Table 4. H₂O₂ production and pollutant removal rate after carbon material deposition in GF substrate.

Samples	Modification conditions	H ₂ O ₂ (mg/L)	Time (min)	C ₀ (mg/L)	Degradation efficiency (%)	Ref.
GF	Carbon Black, polytetrafluoroethylene, n-butanol and deionized water are mixed in an ultrasonic bath to create a uniform suspension. Then, the graphite felt is immersed in the mixture and subjected to ultrasonic treatment and then dried.	197.6	90	-	98.2	[73]
MWCNTs-CB/GF	GF was immersed in a solution containing MWCNT, CB, 60% PTFE, ethanol and ultra-pure water for ultrasonic treatment, then dried for 12 h and finally annealed at 360°C for 30 minutes.	309	120	100	98.7	[72]
GF-(1:5)	The mass ratio of carbon black and PTFE is 1:5	472.9	60	50	100 (15min)	[68]
G-N-2.0	PTFE emulsion with a mass ratio of 1:2 graphite / PTFE and an appropriate amount of ethanol were ultrasonic treated at room temperature for 20 min.	104	120	-	-	[74]
GR/C	Graphene was added to a solution of n-methyl-2-pyrrolidone. The graphite felt was then immersed in the solution and baked for 2 h to make the powder firmly adhere to the graphite felt.	13.6	30	5	>80	[75]

graphene. The specific surface area and pore volume of the cathode are 2.5 and 11.2 times of those of the GF cathode. By CV analysis, the existence of graphene accelerates the electron transfer rate and is beneficial to ORR, which contributes to the increase of H₂O₂ production. A series of organic pollutants (Orange II, Methylene blue, sulfadiazine and phenol) were degraded by EF and all organic compounds were completely removed within 1 hour, the modified cathode has obvious effect of degrading organic matter in EF.

CNTs are another common one-dimensional carbon material, which can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) according to the number of layers. Previous studies have shown that CB greatly improves the production of H₂O₂. Therefore, Pan et al. [72] prepared GF cathode modified by MWCNTs and CB. MWCNT-CB /GF surface contains uniform MWCNT and CB, and the porous structure of GF surface promotes the diffusion of O₂. It is observed that MWCNT-CB/GF has higher response current and lower initial potential in LSV. This indicates that the conductivity of the electrode increases, and the catalytic oxidation activity increases, which accelerates the generation of H₂O₂ and the removal of pollutants.

Change the Wettability of the Electrode

One property of solid surface is wettability, and the contact angle is usually used as a parameter to study wettability. The surface of the material is considered hydrophilic when the gas-liquid-solid interface is less than 90°, and hydrophobic when the gas-liquid-solid interface is more than 90°. The wettability of the electrode surface affects the electrochemical

performance by affecting the mass transfer of the electrode. The key is to change the wettability of the electrode surface. The modification method is simple and only modulates the hydrophilic and hydrophobic properties of the electrode material to achieve efficient H₂O₂ production. The mechanism of H₂O₂ generation by hydrophilic, hydrophobic, and Janus GFs is depicted in Fig. 5.

Hydrophilic Electrodes

The hydrophilicity and hydrophobicity of the electrode are important for the production of H₂O₂. The low content of hetero-atoms in GF results in high hydrophobicity and low activity of the material. As shown in Fig. 4a), the increase in the hydrophilicity of the electrode promotes electron transfer between the electrode and the electrolyte, thus increasing the electrocatalytic activity. The hydrophilicity of the electrode was mainly improved by introducing oxygen-containing functional groups, in which only dissolved oxygen was used to increase H₂O₂ production. In general, the higher the hydrophilicity, the faster the diffusion rate of O₂, resulting in more H₂O₂. Ou et al. [76] obtained M-GF (modified by concentrated H₂SO₄, NaNO₃ and KMnO₄) by chemical modification. In order to study the wettability of GF before and after modification, their contact angles were measured. The contact Angle of M-GF is 61.5°, while the contact Angle of GF is 120.3°. This result shows that the hydrophilicity of M-GF is greatly improved after chemical modification. The O/C of M-GF is 0.303, which is increased by 0.248 compared with before modification, indicating that the increase of oxygen content is of great help to the improvement of hydrophilicity.

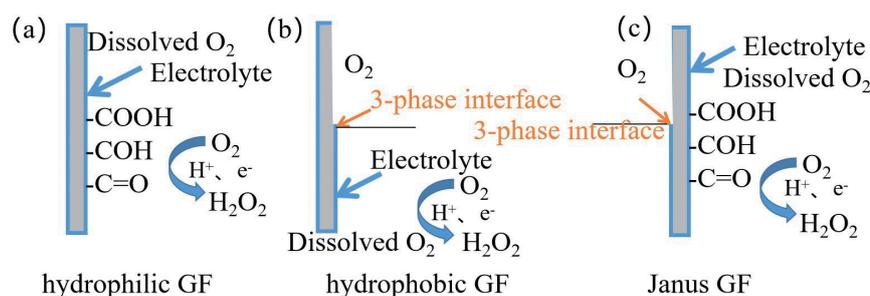


Fig. 5. Mechanism of H_2O_2 generation by hydrophilic, hydrophobic and Janus GFs.

Hydrophobic Electrodes

To improve the hydrophobicity of the electrode, an adhesive is used to connect the electrode to the substrate. The common adhesives are PTFE and polyvinylidene fluoride (PVDF), which allow the gas to contact the solution on the electrode surface through the pores of the electrode, the addition of the binder also creates many active sites to increase ORR to produce more H_2O_2 . As shown in Fig. 4b), the hydrophobic electrode is the key to the formation of a stable three-phase interface, where oxygen enters from the pores and the solution is isolated from the pores. This improves the ORR reaction to produce H_2O_2 . Ren et al. [73] deposited a mixture of CB, PTFE emulsion and ethanol onto the GF surface and measured the contact angle and found that before modification the GF was hydrophilic and after modification the contact angle of the GF was measured to be 138° . Also this study found that the surface area of the modified GF increased from $3.95 \text{ m}^2/\text{g}$ to $9.48 \text{ m}^2/\text{g}$ and the pore volume increased from $0.0026 \text{ cm}^3/\text{g}$ to $0.31 \text{ cm}^3/\text{g}$, where the number of micro and mesopores increased significantly and the

micro and surface structural changes increased the H_2O_2 production, the same situation occurred for the study of the current efficiency, which was 7.26% for the GF before and after the modification and 63.56%. These results can be explained by the increased number of micropores and mesopores and the enhanced hydrophobicity of the electrode surface. Zhou et al. [49] soaked GF in 30 wt% PTFE to obtain hydrophobicity GF-P-2. In the SEM image, it was observed that the graphite fiber was wrapped by PTFE, and some PTFE was filled in the space, which significantly changed the hydrophilicity of GF. O_2 bubbles formed a three-phase interface around PTFE and produced more H_2O_2 .

Janus Electrodes

Some researchers have combined the advantages of hydrophobic and hydrophilic electrodes to develop asymmetric wettability (Janus) electrodes that contain both hydrophilic and hydrophobic properties, with ion transfer in the hydrophilic layer and a stable gas layer in the hydrophobic water. As in Fig. 4c), both of the above H_2O_2 generation mechanisms are

Table 5. Compares the performance of different wettability electrodes.

Samples	Modification conditions	H_2O_2 (mg/L)	CE (%)	Ref.
Hydrophilic				
HIE	The OCB in 8% PVDF/DMA solution was fully mixed and then evenly coated on one side of the original GF. The catalyst of GF was immersed in water for 30 min to remove the solvent. GF was dried overnight to obtain hydrophilic electrode.	2.8 ± 0.1	21.9 ± 0.6	[77]
GF-I-3	GFs was modified in 50 mM Na_2SO_4 electrolyte at 200 mA for 30 min.	46.8	15.9	[49]
Hydrophobic				
HOE	The graphite felt substrate was immersed in 6% PTFE solution and then treated in a furnace at 350°C . It is then cooled in a furnace to room temperature.	25.1 ± 6.4	96.5 ± 0.2	[77]
GF-(1:29)	GF was immersed in a mixture of 60% PTFE and 3.25 mL deionized water, dried at 80°C and annealed at 350°C for 24 h.	29.6	6.1	[78]
Janus electrodes				
Janus-1	After hydrophobic treatment, OCB of 8% PVDF/DMA solution was added into GF and mixed thoroughly, and then evenly coated on one side of the original GF	62.1 ± 2.6	90.1 ± 2.5	[77]
GF-J	The Janus GF electrode was prepared by coating PTFE only on the lower half of the GF electrode.	49.7	-	[49]

present, and electrodes with increased 2-electron ORR have been prepared through three-phase interfacial oxygen transfer, where the hydrophilic part can utilise dissolved oxygen and O_2 generated by the anode. The electrode prepared by Zhou et al. [49] is hydrophilic in the upper part and hydrophobic in the lower part. So that the O_2 bubbles confined in the hydrophobic zone can reach the hydrophilic zone, CV shows that Janus electrode exhibits better current response and better cycling stability than GF before modification. The H_2O_2 production of hydrophilic electrode, hydrophobic electrode and Janus electrode were compared under the same conditions, Janus electrode produces 49.7 mg/L more than hydrophobic electrode 48.8 mg/L and hydrophilic electrode 46.8 mg/L, and the H_2O_2 produced by preparing Janus electrode is higher than hydrophilic or hydrophobic electrode. Wang et al. [77] prepared the Janus electrode in order to solve the problem of low O_2 transfer efficiency and utilization efficiency, which is hydrophilic on one side and hydrophobic on the other. Also superior to other single wetting electrodes, Janus electrodes reduce O_2 transfer limitations and are used in practical applications at lower cost.

Other Modification Methods

GF electrode was modified by ionomer. Chou et al. [79] modified GF by impregnating Nafion ionomer solution to improve the wettability and electrocatalytic activity of the cathode. The results showed that no surface functional groups were formed except the sulfonic groups in the ionomer. At the same time, graphitization of electrode surface is improved by applying electric field, thereby increasing electrode activity.

Metal oxides with low cost, low impact on the environment and excellent electrocatalytic performance have also received attention from modified carbon materials. Wang et al. [80] loaded cerium oxide on GF surface by hydrothermal method to obtain CeO_x /GF. After characterization, it was found that CeO_x enhanced the surface hydrophilicity and reduced the resistance of GF. In the E-peroxone (EP) process, more O_2 is transferred to the electrode surface, and the utilization rate of O_3 is improved by this process. Carbamazepine mineralization reaches 69.4% within 60 min, and the degradation efficiency of TOC is not affected in a wide pH range of 5-9.

Electrode polarity reversal is a technique for the polarity exchange of two electrodes at a specified operating interval [81]. Zhou et al. [82] modified GF in situ with electrode polarity interchange technology to achieve in-situ modification of GF under conditions of low acid and low conductivity. The modified GF increases the oxygen-containing groups, surface hydrophilicity and high yield of H_2O_2 at neutral pH and low conductivity conditions. At the same time, the stability of the modified GF was studied. After 30

consecutive tests of the GF, the production of H_2O_2 decreased, but after the secondary modification through electrode polarity swap, the production of H_2O_2 reached the optimal value again.

Conclusions and Prospects

The application of modified GF to increase H_2O_2 production and degradation of organic pollutants in water in recent years is reviewed. A variety of modification methods were designed for GF modification, such as the introduction of oxygen-containing functional groups, heteroatomic doping, deposition of carbon materials, and hydrophilic and hydrophobic modification to improve ORR, generate more H_2O_2 , and generate more oxidizing $\cdot OH$ in EF for efficient degradation of organic pollutants. Considering the disadvantages of pH in EF reactions, methods to treat contaminants in a wider pH range were sought; Further research on the improvement of the new reactor, more efficient removal of pollutants; Several modification methods were applied to the degradation of the same pollutant, and the modification method with the lowest cost and the best degradation effect was selected. And how to use the reducing property of the hydrogen active free radical generated by the cathode to degrade the organic pollutants will be the future research hotspot and direction. For example, the following research content:

1. Introduce the cutting-edge hot spot modification technology in the field of fuel cells and catalysts into the field of gas diffusion cathode modification to further improve the H_2O_2 production of graphite felt;
2. At present, the stability of the modified electrode is relatively poor, which needs to be further improved in the actual industrial application;
3. The optimal pH degradation of EF is limited to the range of 2.8-3.5. Combined with electrocoagulation and E-peroxone process, it is expected to degrade pollutants rapidly in a wider pH range and at low energy consumption/cost;
4. Strengthen the properties of cathode reduction, study the mechanism of electric reduction, master the mechanism of pollutant degradation by electric reduction, and expect more efficient pollutant degradation performance by using hydrogen reduction free radicals;
5. Expand the application range of modified graphite felt. At present, there are few researches on the removal of gaseous pollutants and heavy metals.

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Conflict of Interest

The authors declare no conflict of interest.

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