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Article

N-doped carbon-coated Fe₃N composite as heterogeneous electro-Fenton catalyst for efficient degradation of organics

Juan Xiao, Junwei Chen, Zuqiao Ou, Junhang Lai, Tongwen Yu, Yi Wang *

The Key Laboratory of Low-Carbon Chemistry & Energy Conservation of Guangdong Province, School of Chemical Engineering and Technology, School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou 510275, Guangdong, China

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ABSTRACT

Herein, the application of a N-doped graphitic-carbon-coated iron nitride composite dispersed in a N-doped carbon framework (Fe₃N@NG/NC) is investigated as a heterogeneous electro-Fenton (HE-EF) catalyst for the efficient removal of organics. The simultaneous carbonization and ammonia etching of iron-based metal organic framework (Fe-MOF) materials yielded well-dispersed N-doped carbon-coated Fe₃N nanoparticles with a diameter of ~70 nm. The Fe₃N and pyridinic N endowed the composite with high HE-EF activity for decomposing the electrogenerated H₂O₂ to •OH. The Fe₃N@NG/NC exhibited outstanding HE-EF performance in removing various organic pollutants with low iron leaching. A removal rate of 97–100% could be obtained for rhodamine B (RhB), dimethyl phthalate, methylene blue, and orange II in 120 min at a pH of 5.0. When the solution pH was set to 3.0, 5.0, 7.0, and 9.0, the removal rate of RhB reached 100%, 96%, 92%, and 81%, respectively, in 60 min at an optimum voltage of 0.0 V (vs. reversible hydrogen electrode (RHE)). Moreover, the concentration of leached iron was expected to be below 0.03 mg/L in a wide pH range of 3.0–9.0. In addition, the RhB removal efficiency remained as high as 90% after six cycles in the reusability experiments. This work highlights the MOF-derived Fe₃N composite as an efficient HE-EF catalyst and the corresponding catalytic mechanism, which facilitates its application in wastewater treatment.

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1. Introduction

The electro-Fenton process is an effective technology for treating organic pollutants by reacting the dissolved Fe(II) with H₂O₂ electrogenerated from the two-electron oxygen reduction reaction (2e⁻ ORR) on the cathode material, as expressed in Eq. (1) [1–3]. In homogeneous electro-Fenton (HO-EF) reactions, iron sludge is easily formed due to the precipitation of

dissolved Fe(II) at high pH values (pH > 4.0), thereby limiting the application of HO-EF in wastewater treatment [4,5]. Iron-containing solid catalysts are often used to widen the working pH range during heterogeneous electro-Fenton (HE-EF) processes [6–9]. The electrogeneration of H₂O₂ and the activation of H₂O₂ toward hydroxyl radicals (•OH) occur simultaneously on the surface of the catalyst-containing cathode during the HE-EF process [8,9].

* Corresponding author. Tel/Fax: +86-20-84113253; E-mail: wangyi76@mail.sysu.edu.cn

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A series of iron-based catalysts, such as Fe_3O_4 , Fe_2O_3 , FeOOH , FeS_2 , and their composites, have been used for the HE-EF process [10–14]. These Fe-containing materials are commonly immobilized on various support materials to form Fe-loaded structures for decreasing iron leaching; examples of the support materials include Fe-carbon aerogels, Fe-activated carbon fibers, Fe-carbon nanotubes, Fe-graphene, Fe-zeolite and Fe-kaolin [15–20]. It is noteworthy that the utilization of metal and nonmetal ion-doped Fe-based composites is an effective strategy for further enhancing the HE-EF performance. Some metal elements with variable valences, such as Cu, Mn, and Co, are doped into Fe-based catalysts for the construction of dual reaction centers with strong electronic interactions and synergistic effects, thereby enabling more efficient H_2O_2 activation when compared to that achieved using a single reaction center [21–24]. The generation and activation of H_2O_2 can be improved by nonmetal doping of carbon-based materials, such as F, N, O, S, P, and multiple heteroatoms [25–28]. However, easy agglomeration, uneven distribution of iron particles, and iron leaching are problems that still need to be solved. Simultaneously, the HE-EF performance of the iron-carbon composites is weakened to some extent because of the low iron content. Therefore, it is desirable to develop a stable and well-dispersed catalyst with high $2e^-$ ORR properties and high H_2O_2 activation, which are two crucial factors for enhancing the HE-EF performance in the degradation of organic pollutants.

Iron-based metal organic framework (Fe-MOF)-derived materials, which can be obtained by pyrolyzing Fe-MOF materials, have been applied to wastewater treatment because of their large surface area, regular porous structure, well-dispersed metal sites, and good conductivity and stability [29–31]. Several Fe-MOF derivatives, such as nano-ZVI/C, FeO_x/NC , FeS_2/C , $\text{Mn}/\text{Fe}/\text{C}$, and $\text{Fe}/\text{Cu}/\text{NC}$, have been recently utilized for the removal of organic matter in the HE-EF reaction [23,32–35]. Iron oxides are the main forms of iron species in these Fe-based composites, which exhibit difficulty in preventing the leaching of iron ions. Therefore, the development of Fe-MOF-derived alloy materials such as FeC_x/C and FeN_x/C is required to further improve the stability and anticorrosion performance, and thereby broaden the application of Fe-MOF in wastewater treatment.

Herein, we constructed a N-doped carbon-coated iron nitride composite ($\text{Fe}_3\text{N@NG/NC}$) via the simultaneous carbonization and ammonia etching of a hydrothermally prepared Fe-MOF. The HE-EF degradation of rhodamine B (RhB) as a model contaminant was evaluated in detail using $\text{Fe}_3\text{N@NG/NC}$ as the HE-EF catalyst. The physicochemical properties of $\text{Fe}_3\text{N@NG/NC}$ were characterized and linked to their HE-EF performance. Moreover, the reusability of the composite and its application in treating other organic pollutants were examined. Furthermore, a possible HE-EF mechanism was tentatively explored.

2. Experimental

2.1. Chemicals

Terephthalic acid (TA), ferric chloride (hexahydrate, FeCl_3), 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and HPLC-grade methanol were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Further, *N,N*-dimethylformamide (DMF), absolute ethyl alcohol (EtOH), RhB, methylene blue, orange II, dimethyl phthalate, NaOH, KOH, H_2SO_4 , and Na_2SO_4 were purchased from Damao Chemical Reagent Factory. Graphite felt (GF) was purchased from Beijing Jinglong Special Carbon Technology Co., Ltd. The raw GF was degreased and purified using acetone, KOH (1.0 M), and deionized water [36].

2.2. $\text{Fe}_3\text{N@NG/NC}$ synthesis and HE-EF cathode construction

The $\text{Fe}_3\text{N@NG/NC}$ catalyst was obtained through the pyrolysis of the Fe-MOF material, which was followed by ammonia etching [37]. A mixture of FeCl_3 (2.703 g), TA (1.661 g), and DMF (60.0 mL) was stirred for 30 min to obtain a uniform solution, which was transferred to a Teflon-lined autoclave and subjected to solvothermal treatment at 100 °C for 24 h. The brown solid of Fe-MOF was washed and dried at 80 °C for 12 h under vacuum. Then, Fe-MOF (1.000 g) was heated to 750 °C at a heating rate of 10 °C/min in a nitrogen atmosphere; the temperature of 750 °C was maintained for 1 h under flowing ammonia gas and subsequently decreased to room temperature in a nitrogen atmosphere. A black powder was obtained and denoted as $\text{Fe}_3\text{N@NG/NC}$. To explain the HE-EF degradation mechanism, the annealing products of Fe-MOF at 600 and 900 °C were obtained via the same pyrolysis procedure as that used for the $\text{Fe}_3\text{N@NG/NC}$ catalyst at 750 °C. The annealing products of Fe-MOF were also obtained at 750 °C for 1 h in a nitrogen atmosphere. To construct the HE-EF cathode, the catalyst (10.0 mg) was dispersed in EtOH (1.20 mL), deionized water (0.60 mL), and Nafion® solution (5 wt%, 0.20 mL) and then sonicated for 30 min to form a uniform ink, which was coated onto treated GF (catalyst loading: 2.0 mg/cm²).

2.3. Characterizations

X-ray diffraction (XRD) patterns were obtained using a D-MAX 2200 VPC diffractometer with $\text{Cu K}\alpha$ radiation. Scanning electron microscopy (SEM) micrographs were obtained using a Zeiss Gemini SEM500 microscope equipped with a Bruker Flat-Quad energy dispersive spectroscopy (EDS) detector. Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai G2 Spirit transmission electron microscope. X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were performed using an ESCALAB 250 spectrometer and a Renishaw inVia microscope, respectively.

2.4. Rotating ring-disk electrode (RRDE) measurements

RRDE measurements were conducted on an Auto84480 electrochemical station. The Pt ring was polarized at 0.9 V (vs. Ag/AgCl) in a Na_2SO_4 solution (0.1 M, pH 5.0). The H_2O_2

selectivity ($\text{H}_2\text{O}_2\%$) and electron transfer number (n) were calculated using Eqs. (2) and (3) as follows:

$$\text{H}_2\text{O}_2\% = (4 - n) / 2 \quad (2)$$

$$n = (4 \times I_D) / (I_D + I_R/N), \quad (3)$$

where N is the H_2O_2 collection efficiency ($N = 0.37$), I_D is the disk current density, and I_R is the ring current density [38].

Prior to conducting the RRDE measurements, the Ag/AgCl reference electrode was corrected by referring to a commercial reversible hydrogen electrode (RHE; ALS 013373 RHEK) (Fig. S1). The relevant electrode potentials were calculated using Eq. (4) as follows:

$$E(\text{RHE}) = 0.197 + E(\text{Ag}/\text{AgCl}) + 0.0591 \times \text{pH}. \quad (4)$$

2.5. HE-EF degradations

HE-EF degradations were performed using a three-electrode system in an H-type electrolytic cell. A Pt sheet, catalyst-coated GF, and Ag/AgCl were adopted as the counter electrode (anode), working electrode (cathode), and reference electrode in a Na_2SO_4 solution, respectively. NaOH or H_2SO_4 aqueous solutions were added to the Na_2SO_4 solution to obtain the desired pH values before the reaction. RhB, orange II, methylene blue, and dimethyl phthalate were used as the model pollutants to determine the HE-EF performance of the $\text{Fe}_3\text{N}@\text{NG}/\text{NC}$ catalyst. Prior to the HE-EF reaction, a Na_2SO_4 solution (0.1 M) containing organic pollutants (10.0 mg/L) was bubbled with oxygen gas (0.025 m^3/h) for 30 min to obtain an O_2 -saturated solution. Then, a working potential from -0.2 to 0.2 V was applied at the cathode. The reaction solutions were collected at several time intervals and immediately quenched. The concentrations of RhB, orange II, and methylene blue were analyzed using a TU1910 ultraviolet-visible (UV-Vis) spectrophotometer at 554, 484, and 664 nm, respectively. The dimethyl phthalate concentration was detected by a 1260 Infinity II high-performance liquid chromatography system

with the UV absorption detector set at 276 nm. The mobile phase contained methanol and water in a 50:50 volume ratio. The consecutive recycling tests for RhB degradation were conducted to evaluate the reusability of $\text{Fe}_3\text{N}@\text{NG}/\text{NC}$. Released iron ions and electrogenerated H_2O_2 were analyzed on the UV spectra at 510 and 405 nm using the o-phenanthroline and potassium titanium oxalate methods, respectively [39]. Iron leaching was detected using an Optima 8300 inductively coupled plasma optical emission spectrometer. The degradation intermediates were analyzed using a Finnigan Voyager liquid chromatography-mass spectrometry system. The generation of $\cdot\text{OH}$ was detected in the HE-EF system using electron paramagnetic resonance (EPR; A300) with DMPO as a radical scavenger. An Elementar Acquray TOC analyzer was used to detect the total organic carbon (TOC) of the HE-EF systems.

3. Results and discussion

3.1. Catalyst characterization

A schematic diagram for constructing $\text{Fe}_3\text{N}@\text{NG}/\text{NC}$ with Fe_3N particles, a N-doped graphitic carbon (NG) structure, and a N-doped carbon (NC) framework is illustrated in Fig. 1(a). Briefly, Fe-MOF with a MIL-101 structure was successfully prepared owing to the consistent diffraction peaks between the synthesized Fe-MOF and the simulated MIL-101 (Fe), as shown in Fig. 1(b) [40]. $\text{Fe}_3\text{N}@\text{NG}/\text{NC}$ can be successfully fabricated using the one-step calcination of Fe-MOF at 750°C under flowing ammonia gas. The XRD patterns of $\text{Fe}_3\text{N}@\text{NG}/\text{NC}$ in Fig. 1(c) reveal characteristic diffraction peaks at 30.0° , 38.0° , 41.2° , 43.4° , 57.3° , 68.7° , and 76.5° , corresponding to the (101), (110), (002), (111), (112), (300), and (113) planes of hexagonal Fe_3N (JCPDS No. 83-0879), respectively. Compared with the Fe_3N peaks at 30.0° , 38.3° , 41.3° , 43.8° , 57.6° , 69.3° , and 77.0° , some

Fig. 1. (a) Schematic diagram of the synthesis procedure used for $\text{Fe}_3\text{N}@\text{NG}/\text{NC}$; XRD patterns of MIL-101 (Fe) (b) and $\text{Fe}_3\text{N}@\text{NG}/\text{NC}$ (c).

Fig. 2. SEM (a) and corresponding elemental mapping (b–d) images of $\text{Fe}_3\text{N@NG/NC}$.

of the $\text{Fe}_3\text{N@NG/NC}$ peaks are slightly shifted to the left, which is possibly due to the inevitable in situ carbon doping [41]. Moreover, a weak peak is observed at 22.8° and ascribed to the (002) plane of graphitic carbon. This peak has clearly moved to the left as compared to the peak at 25° in the standardized patterns of graphitic carbon; this is probably due to the doping of N into carbon [42]. The above observations indicate that the $\text{Fe}_3\text{N@NG/NC}$ composite possibly comprises Fe_3N particles and N-doped graphitic carbon.

The morphology of the Fe-MOF is shown in Fig. S2. Fe-MOF has an octahedral structure with an average diameter of 1.0 μm . The morphological structure of $\text{Fe}_3\text{N@NG/NC}$ differs significantly from that of Fe-MOF. As depicted in Fig. 2 and Fig. S3, $\text{Fe}_3\text{N@NG/NC}$ shows a three-dimensional porous structure, and Fe_3N particles are uniformly dispersed in the NC framework. Furthermore, the elemental mapping images confirm that C, N, and Fe are uniformly distributed. The EDX spectrum of $\text{Fe}_3\text{N@NG/NC}$ is plotted in Fig. S4, which further exemplifies the presence of C, N, and Fe in the composite, in addition to the adsorbed oxygen on the surface of the composite and Al from the substrate.

As shown in Fig. 3(a) and (b), the images obtained via high-angle annular dark-field scanning TEM (HAADF-STEM) and TEM further verify that numerous Fe_3N particles with an average diameter of 70 nm are uniformly dispersed in the NC frameworks. The high-resolution TEM (HRTEM) images show

Fig. 3. HAADF-STEM (a), TEM (b), HRTEM (c), and atomic-resolution HRTEM (d) images of $\text{Fe}_3\text{N@NG/NC}$.

that Fe_3N nanoparticles are coated in N-doped graphitic carbon layers with well-defined lattice fringes that are 0.39 and 0.41 nm larger than that of graphite (0.33 nm) due to N species doping (Fig. 3(c)) [43]. The interplanar spacings of 0.21 and 0.23 nm can be ascribed to the (111) and (110) planes of hexagonal Fe_3N (PDF No. 83-0879) with an internal angle of $\sim 90^\circ$ (Fig. 3(d)). These results confirm that graphitic-carbon-coated Fe_3N nanoparticles are dispersed in the NC framework in the $\text{Fe}_3\text{N@NG/NC}$ composite. Notably, the graphitic-carbon-coated structure can effectively prevent the dissolution and aggregation of Fe_3N nanoparticles. In addition, the intimate contact between the NC framework and graphitic-carbon-coated Fe_3N can improve the electron transfer in the $\text{Fe}_3\text{N@NG/NC}$ composite during the electrochemical process.

To gain insight into the surface chemical composition of the $\text{Fe}_3\text{N@NG/NC}$ composite, XPS and Raman spectra have been elucidated in Fig. 4. The two characteristic peaks at 711.1 and 724.5 eV and the two weak satellite peaks at 719.6 and 732.6 eV in the Fe 2p spectra are ascribed to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively (Fig. 4(a)) [44]. The two peaks at 711.1 and 724.5 eV are deconvoluted into five peaks at 709.4, 711.3, 723.9, 713.6, and 725.8 eV; these peaks reveal the formation of Fe–N and the presence of Fe(II) and Fe(III), respectively [45]. Moreover, the N 1s XPS spectra and different N species contents are shown in Fig. 4(b) and Fig. S5. The five peaks located at 398.4, 399.3, 400.7, 401.5, and 403.7 eV are ascribed to Fe–N (17.0%), pyridinic N (16.9%), pyrrolic N (25.5%), graphitic N (26.5%), and oxidative N (14.2%), respectively [45]. Notably, graphitic N and pyridinic N have been confirmed as active sites for the electrogeneration of H_2O_2 and the activation of H_2O_2 toward $\cdot\text{OH}$, respectively [46,47]. Fig. 3(c) shows that the C 1s XPS spectrum can be divided into three main peaks: C=O (287.9 eV), C–N (285.4 eV), and C–C (284.6 eV); these peaks indicate the carbon encapsulation with N and O doping [42,43,48].

In addition, Fig. 4(d) shows the Raman spectrum of $\text{Fe}_3\text{N@NG/NC}$. Two characteristic peaks of disordered sp^3 -hybridized carbon (D band, 1340 cm^{-1}) and sp^2 -bonded graphite carbon (G band, 1600 cm^{-1}) reveal the presence of graphitic carbon in $\text{Fe}_3\text{N@NG/NC}$. The intensity ratio of the D and G bands (I_D/I_G) can be used to evaluate the degree of graphitization and defect formation in carbonaceous materials [37]. The I_D/I_G value of $\text{Fe}_3\text{N@NG/NC}$ is 0.95, thereby suggesting the presence of highly graphitic carbon that exhibits good conductivity in the $\text{Fe}_3\text{N@NG/NC}$ composite [45]. These

Fig. 4. Fe 2p (a), N 1s (b), C 1s (c) XPS spectra, and Raman spectrum (d) of $\text{Fe}_3\text{N@NG/NC}$.

results confirm that the $\text{Fe}_3\text{N@NG/NC}$ composite contains NG, NC, and Fe_3N , which is consistent with the XRD patterns and the SEM and TEM images. Thus, $\text{Fe}_3\text{N@NG/NC}$ may be a promising electrocatalyst in the HE-EF reaction for effectively degrading organic pollutants.

The ORR activity of the $\text{Fe}_3\text{N@NG/NC}$ composite was evaluated based on RRDE measurements. The polarization curves, H_2O_2 selectivity, and electron transfer number (n) are shown in Fig. 5. The ring current density at -0.3 V is 0.84 mA/cm^2 , which is significantly lower than the disk current density (3.23 mA/cm^2). The corresponding n and H_2O_2 selectivities were calculated to be approximately 2.35–2.50 and 82.2–74.5 at -0.3 to 0.1 V, respectively, suggesting that the 2e^- pathway is dominant during the ORR process at $\text{Fe}_3\text{N@NG/NC}$. Moreover, the concentration of H_2O_2 was detected in the GF- and $\text{Fe}_3\text{N@NG/NC/GF}$ -based systems, as shown in Fig. S6. For

$\text{Fe}_3\text{N@NG/NC/GF}$, the concentration of H_2O_2 was 49.3 mg/L in 60 min, which is almost three times higher than that of the raw GF system (13.6 mg/L). These results verify that $\text{Fe}_3\text{N@NG/NC}$ as a 2e^- ORR electrocatalyst can produce H_2O_2 with the desirable selectivity and production capability.

3.2. HE-EF performance evaluation

As stated earlier, the $\text{Fe}_3\text{N@NG/NC}$ composite can increase the stability of Fe_3N and prevent iron leaching due to the NG-coated Fe_3N structure. It can also increase the utilization rate of Fe_3N by virtue of the high dispersity of Fe_3N in the NC framework, which is expected to work efficiently for both the electrogeneration and activation of H_2O_2 to generate $\cdot\text{OH}$ during the HE-EF process. To confirm this expectation, the behaviors of $\text{Fe}_3\text{N@NG/NC}$ were examined in different HE-EF

Fig. 5. RRDE polarization curves (a), n and H_2O_2 selectivity (b) of $\text{Fe}_3\text{N@NG/NC}$ at pH 5.0. Experimental conditions: scan rate of 10 mV/s , rotation rate of 1600 rpm , and $[\text{Na}_2\text{SO}_4] = 0.1$ M.

Fig. 6. RhB degradation efficiency (a) and corresponding k values (b) of different systems at a pH of 5.0. The effects of pH (c) and working potential (d) on RhB degradation. Experimental conditions: [RhB] = 10.0 mg/L, potential of 0.0 V, and [loaded catalyst] = 2.0 mg/cm².

reaction systems, and the effects of the working potential, pH, and RhB concentration on RhB degradation were evaluated.

As illustrated in Fig. 6(a), the removal of RhB via various reaction systems was investigated. Specifically, the HE-EF degradation of RhB yielded a removal rate of 96% within 60 min at a pH of 5.0. Further proof of the effective removal could be obtained from the UV spectra (Fig. S7), with a rapid decrease in the absorbance of the RhB solution along with the progression of the HE-EF reaction. In contrast, through the adsorption process alone, Fe₃N@NG/NC exhibited a low removal rate of only 8% within 60 min. In the case of the O₂-driven oxidation and the electrogenerated H₂O₂ (EG-H₂O₂)-driven oxidation, the RhB removal rates at the same time were 16% and 28%, respectively. Moreover, it was found that a RhB removal rate of 38% could be obtained in the electrocatalysis process (N₂ instead of O₂). The pseudo first-order rate constants (k) were calculated to be 0.001, 0.003, 0.005, 0.008, and 0.057 min⁻¹ for adsorption, O₂ oxidation, EG-H₂O₂ oxidation, electrocatalysis, and HE-EF, respectively (Fig. 6(b)), thereby indicating that the RhB removal efficiency in the HE-EF system is clearly superior to that of the other systems. Moreover, it should be noted that in the case of a N₂ atmosphere, the as-prepared Fe-MOF-N sample contained Fe, Fe₂O₃, and Fe₃O₄ (Fig. S8(a)). As shown in Fig. S8(b), k of Fe-MOF-N is 0.011 min⁻¹, which is lower than that of Fe-MOF-NH (Fe₃N@NG/NC, 0.057 min⁻¹). This suggests that the HE-EF performance of Fe-MOF-NH (Fe₃N@NG/NC) is superior to that of Fe-MOF-N.

The effects of the pH, working potential, and RhB concentration on RhB degradation were systematically evaluated in the Fe₃N@NG/NC-based HE-EF system. As shown in Fig. 6(c) and Fig. S9(a), the removal rates and corresponding k values of RhB within 60 min are 100%, 96%, 92%, and 81% and 0.076, 0.057, 0.041, and 0.023 min⁻¹ at pH values of 3.0, 5.0, 7.0, and 9.0, respectively, which may be because the

oxidation potential of $\cdot\text{OH}$ at a low pH is higher than that of the high pH system [49]. The RhB degradation efficiency at a pH of 3.0 is the highest, which agrees with the results reported in the literature [15,50,51]. It should be noted that an extremely low iron leaching rate (0–0.03 mg/L) was obtained at a pH of 3.0–9.0 in 60 min, suggesting the high stability of Fe₃N@NG/NC over a wide pH range (Fig. S10). Moreover, a certain amount of H₂O₂ (58.8–116.3 mg/L) could still be detected in 60 min, indicating that RhB can be continuously degraded with increasing reaction time. For the effect of the working potential, the RhB removal rate within 60 min and the corresponding k value at 0.2 V reached 85% and 0.031 min⁻¹, respectively, as shown in Fig. 6(d) and Fig. S9(b). When the working potential was shifted to 0.0 and -0.2 V, the RhB removal rate increased to 96% and 93%, and the k value increased to 0.057 and 0.050 min⁻¹, respectively. The decline in the RhB removal efficiency at -0.2 V can possibly be ascribed to the competitiveness of the hydrogen evolution reaction at the cathode [36]. Thus, the optimal working potential of the HE-EF system is 0.0 V. In addition, the RhB removal rate and kinetic reaction rate constant are inversely proportional to the initial RhB concentration (Fig. S11). A possible explanation for this phenomenon is the coverage of active sites on the catalyst and the undesirable competitive consumption of $\cdot\text{OH}$ in a higher RhB concentration system [52]. Furthermore, a comparison of the RhB removal rate and iron leaching of Fe₃N@NG/NC with other reported heterogeneous catalysts during the HE-EF process is shown in Table S1. Fe₃N@NG/NC clearly exhibits a higher RhB removal rate; however, the lower iron leaching is obviously superior to that of the majority of the other catalysts. Thus, these results reveal that Fe₃N@NG/NC exhibits outstanding HE-EF performance for RhB removal at a wide pH range.

The reusability and stability of Fe₃N@NG/NC were investigated by studying the results of the recycling tests for

Fig. 7. Results of the recycling tests for HE-EF degradation of RhB at a pH of 5.0. Experimental conditions: [RhB] = 10.0 mg/L, potential of 0.0 V, and [loaded catalyst] = 2.0 mg/cm².

the HE-EF degradation of RhB. As shown in Fig. 7, the reaction activity in the sixth cycle is somewhat different from that in the first experiment (96%), while there was 90% degradation of RhB in 60 min. Notably, released iron ions were detected in the six cycling tests, with concentrations of 0.010, 0.024, 0.028, 0.036, 0.046, and 0.055 mg/L in the first, second, third, fourth, fifth, and sixth tests, respectively. The total concentration of released iron ions is below 0.2 mg/L, thereby confirming the high stability of Fe₃N@NG/NC in the HE-EF system. Moreover, the XPS spectra of Fe₃N@NG/NC after the HE-EF reaction were obtained for further evaluation of its stability, as shown in Fig. S12. The contents of Fe(II), graphitic N, and pyridinic N of the used Fe₃N@NG/NC were 51.5%, 22.0%, and 13.2%, respectively, which are slightly lower values than those of fresh Fe₃N@NG/NC (52.9%, 26.5%, and 16.9%, respectively). This is because Fe(II) and pyridinic N can be oxidized to form Fe(III) and pyridinic N-oxide, respectively, and graphitic N can be cleaved to form pyridinic N and pyrrolic N during the HE-EF process [53]. These results demonstrate that Fe₃N@NG/NC as a HE-EF catalyst possesses good reusability and stability.

To further evaluate the HE-EF performance of Fe₃N@NG/NC, the HE-EF degradation of various organic pollutants was also detected. The removal rates of dimethyl phthalate, RhB, methylene blue, and orange II after 120 min were 100%, 100%, 99%, and 97%, with corresponding *k* of

0.028, 0.039, 0.057, 0.078 min⁻¹, respectively (Fig. 8). The higher degradation kinetics of dimethyl phthalate compared to those of the other organics is possibly due to the easy bond cleavage of the ester group. Moreover, the corresponding TOC removal rates of the above-mentioned organics in 120 min were 65%, 60%, 69%, and 49%, respectively (Fig. S13). Thus, Fe₃N@NG/NC exhibits good HE-EF performance for organics degradation because of the nonselective and strong oxidizing properties of the generated •OH.

3.3. Possible reaction mechanisms

To verify the primary active species in the HE-EF reaction, EPR measurement was performed. A small amount of •OH was obtained in the raw GF-based system (Fig. 9). In the Fe₃N@NG/NC/GF-based system, a curve of quartet characteristic peaks with a 1:2:2:1 intensity ratio was obtained, confirming the formation of •OH [50,54,55]. The produced •OH is probably due to the heterogeneous Fenton reaction between the Fe₃N@NG/NC catalyst and the electrogenerated H₂O₂.

To further demonstrate the HE-EF reaction mechanism of the Fe₃N@NG/NC electrocatalyst, some pyrolytic products of Fe-MOF (FeNC materials) were synthesized using the same pyrolysis procedure except for different calcination temperatures. The XRD patterns, RhB degradation, and XPS spectra of the FeNC materials were also comparatively explored. As shown in Fig. 10(a), the XRD pattern of FeNC-600 at a calcination temperature of 600 °C is similar to that of FeNC-750 (Fe₃N@NG/NC), indicating that these two FeNC materials contain Fe₃N and graphitic carbon. When the calcination temperature was increased to 900 °C, the characteristic diffraction peaks of Fe₃N almost disappeared, and new diffraction peaks emerged at 35.5°, 57.0°, 62.5°, 44.7°, 41.2°, 48.0°, and 70.1°, corresponding to the (311), (511), and (440) planes of Fe₃O₄ (JCPDS No. 19-0629), the (110) plane of Fe (JCPDS No. 06-0696), and the (111), (200), and (220) planes of Fe₄N (JCPDS No. 06-0627), respectively. This suggests that FeNC-900 contains Fe₄N, Fe, Fe₃N, and Fe₃O₄. From Fig. 10(b), the *k* values of FeNC-600, FeNC-750 (Fe₃N@NG/NC), and FeNC-900 as electrocatalysts for the HE-EF degradation of RhB are 0.044, 0.057, and 0.039 min⁻¹, respectively. This can be ascribed to the excessive oxidation of Fe-MOF. Thus, the

Fig. 8. Removal efficiency for organics (a) and corresponding *k* values (b) in the HE-EF reaction at a pH of 5.0. Experimental conditions: [dimethyl phthalate] = [RhB] = [methylene blue] = [orange II] = 10.0 mg/L, potential of 0.0 V, and [loaded catalyst] = 2.0 mg/cm².

Fig. 9. EPR spectra of $\cdot\text{OH}$ in raw GF and $\text{Fe}_3\text{N@NG/NC/GF}$ systems.

optimum calcination temperature was 750 $^{\circ}\text{C}$.

To understand the difference in the RhB removal efficiency, the XPS spectra of these FeNC materials were analyzed. As shown in Figs. 10(c)–(f), for FeNC-750 ($\text{Fe}_3\text{N@NG/NC}$), the contents of Fe(II) and graphitic N are 52.9% and 26.5%, respectively, which are higher than those of FeNC-600 (48.8%, 20.2%) and FeNC-900 (47.0%, 20.6%). The pyridinic N content of FeNC-600 and FeNC-750 ($\text{Fe}_3\text{N@NG/NC}$) was 17.5% and 16.9%, respectively, which was higher than that of FeNC-900 (12.5%). Notably, more amount of graphitic N, pyridinic N, and Fe(II) could increase the working efficiency of FeNC-750 ($\text{Fe}_3\text{N@NG/NC}$) during the HE-EF process via the electrogeneration and activation of H_2O_2 . Moreover, based on the Raman characterization of these FeNC materials (Fig. S14), a higher I_D/I_G value could be obtained for FeNC-750 ($\text{Fe}_3\text{N@NG/NC}$) (0.95) as compared to those of FeNC-600 (0.79) and FeNC-900 (0.93), which may be due to the existence of more structural defects in the graphitic carbon layer. Thus, FeNC-750 ($\text{Fe}_3\text{N@NG/NC}$) with more Fe(II), graphitic N, and

Fig. 11. Possible HE-EF degradation mechanism for RhB with $\text{Fe}_3\text{N@NG/NC/GF}$ as the cathode.

pyridinic N is more favorable for the HE-EF reaction. Moreover, some structural defects can further promote the HE-EF reaction.

Based on the above discussion, a possible HE-EF mechanism for RhB degradation with $\text{Fe}_3\text{N@NG/NC/GF}$ as the cathode is tentatively proposed, as shown in Fig. 11. First, H_2O_2 is electrogenerated via a 2e^- ORR. Subsequently, $\cdot\text{OH}$ is formed via the reaction between Fe(II) and H_2O_2 . Further, Fe(II) can be regenerated by an electron. Afterwards, more $\cdot\text{OH}$ is produced due to the continuous electrogeneration of H_2O_2 and the activation of H_2O_2 toward OH; thus, the HE-EF process can be enhanced. Ultimately, RhB can be gradually decomposed into small molecular acids via chromophore cleavage and ring opening, and further mineralized to CO_2 and H_2O by the continuous generation of $\cdot\text{OH}$ (Fig. S15) [15,56–59].

4. Conclusions

A $\text{Fe}_3\text{N@NG/NC}$ electrocatalyst was fabricated via the one-step carbonization of Fe-MOF under ammonia gas. The uniformly dispersed Fe_3N nanoparticles with a NG-coated structure in the NC framework facilitated efficient electron

Fig. 10. XRD patterns of the FeNC material (a) and k values for the RhB removal (b); (c,d) XPS spectra of Fe and corresponding Fe content of different Fe species; (e,f) N 1s XPS spectra and corresponding N content of different N species (FeNC materials).

transfer and decomposition of H_2O_2 to $\cdot\text{OH}$, which enhanced the HE-EF reaction. The graphitic N and pyridinic N endowed the $\text{Fe}_3\text{N}@ \text{NG}/\text{NC}$ catalyst with further improvement of the HE-EF performance via the electrogeneration and activation of H_2O_2 toward $\cdot\text{OH}$. Thus, the versatile $\text{Fe}_3\text{N}@ \text{NG}/\text{NC}$ exhibited high HE-EF catalytic activity ($k = 0.057 \text{ min}^{-1}$ at pH 5.0), a wide working pH range (3.0–9.0), good reusability (six cycles), and low iron leaching (0–0.03 mg/L) for degrading organics. This work presents a new idea for constructing $\text{Fe}_3\text{N}@ \text{NG}/\text{NC}$ catalysts with excellent HE-EF performance and further expands the application of MOF-based materials in wastewater treatment.

Electronic supporting information

Supporting information is available in the online version of this article.

References

- [1] H. Q. He, Z. Zhou, *Crit. Rev. Environ. Sci. Technol.*, **2017**, 47, 2100–2131.
- [2] Y. Wang, Y. H. Liu, T. F. Liu, S. Q. Song, X. C. Gui, H. Liu, *Appl. Catal. B*, **2014**, 156–157, 1–7.
- [3] J. L. Yu, T. F. Liu, H. Y. Liu, Y. Wang, *Chin. J. Catal.*, **2016**, 37, 2079–2085.
- [4] F. X. Deng, S. X. Li, M. H. Zhou, Y. S. Zhu, S. Qiu, H. K. Li, F. Ma, J. Z. Jiang, *Appl. Catal. B*, **2019**, 256, 117796.
- [5] C. Zhang, G. B. Ren, W. Wang, X. M. Yu, F. K. Yu, Q. Z. Zhang, M. H. Zhou, *Sep. Purif. Technol.*, **2019**, 208, 76–82.
- [6] V. Poza-Nogueiras, E. Rosales, M. Pazos, M. A. Sanromán, *Chemosphere*, **2018**, 201, 399–416.
- [7] X. Ding, S. Y. Wang, W. Q. Shen, Y. Mu, L. Wang, H. Chen, L. Z. Zhang, *Water Res.*, **2017**, 112, 9–18.
- [8] P. Xu, H. Xu, D. Y. Zheng, *Chem. Eng. J.*, **2019**, 361, 968–974.
- [9] S. O. Ganiyu, M. Zhou, C. A. Martínez-Huitle, *Appl. Catal. B*, **2018**, 235, 103–129.
- [10] P. Dong, W. J. Liu, S. J. Wang, H. L. Wang, Y. Q. Wang, C. C. Zhao, *Electrochim. Acta*, **2019**, 308, 54–63.
- [11] Q. S. Peng, H. Y. Zhao, L. Qian, Y. B. Wang, G. H. Zhao, *Appl. Catal. B*, **2015**, 174–175, 157–166.
- [12] Y. Z. Wang, H. M. Zhang, B. K. Li, M. C. Yu, R. Zhao, X. T. Xu, L. Cai, *Chem. Eng. J.*, **2019**, 359, 914–923.
- [13] L. Z. Huang, M. T. Zhu, Z. Z. Liu, Z. P. Wang, H. C. B. Hansen, *J. Hazard. Mater.*, **2019**, 364, 39–47.
- [14] F. K. Yu, Y. Wang, H. R. Ma, M. H. Zhou, *Sep. Purif. Technol.*, **2020**, 248, 117022.
- [15] P. Xu, D. Y. Zheng, Z. Y. Xie, J. W. Ma, J. Yu, B. L. Hou, *Sep. Purif. Technol.*, **2020**, 234, 116103.
- [16] H. Y. Zhao, Q. N. Wang, Y. Chen, Q. L. Tian, G. H. Zhao, *Carbon*, **2017**, 124, 112–122.
- [17] W. Chen, X. L. Yang, J. F. Huang, Y. H. Zhu, Y. Zhou, Y. F. Yao, C. Z. Li, *Electrochim. Acta*, **2016**, 200, 75–83.
- [18] Y. M. Zhang, Z. Chen, P. P. Wu, Y. X. Duan, L. C. Zhou, Y. X. Lai, F. Wang, S. Li, *J. Hazard. Mater.*, **2020**, 393, 120448.
- [19] T. X. Huong Le, M. Drobek, M. Bechelany, J. Motuzas, A. Julbe, M. Cretin, *Microporous Mesoporous Mater.*, **2019**, 278, 64–69.
- [20] A. Özcan, A. Atilir Özcan, Y. Demirci, E. Şener, *Appl. Catal. B*, **2017**, 200, 361–371.
- [21] H. Y. Zhao, L. Qian, Y. Chen, Q. N. Wang, G. H. Zhao, *Chem. Eng. J.*, **2018**, 332, 486–498.
- [22] T. Luo, H. P. Feng, L. Tang, Y. Lu, W. W. Tang, S. Chen, J. F. Yu, Q. Q. Xie, X. L. Ouyang, Z. M. Chen, *Chem. Eng. J.*, **2020**, 382, 122970.
- [23] X. L. Zhou, D. Xu, Y. C. Chen, Y. Y. Hu, *Chem. Eng. J.*, **2020**, 384, 123324.
- [24] S. O. Ganiyu, T. X. Huong Le, M. Bechelany, G. Esposito, E. D. van Hullebusch, M. A. Oturan, M. Cretin, *J. Mater. Chem. A*, **2017**, 5, 3655–3666.
- [25] Y. Wang, M. Yi, K. Wang, S. Q. Song, *Chin. J. Catal.*, **2019**, 40, 523–533.
- [26] K. Zhao, Y. Su, X. Quan, Y. M. Liu, S. Chen, H. T. Yu, *J. Catal.*, **2018**, 357, 118–126.
- [27] V. Perazzolo, C. Durante, R. Pilot, A. Paduano, J. Zheng, G. A. Rizzi, A. Martucci, G. Granozzi, A. Gennaro, *Carbon*, **2015**, 95, 949–963.
- [28] K. Q. Li, J. M. Liu, J. Li, Z. Q. Wan, *Chemosphere*, **2018**, 193, 800–810.
- [29] M. Cheng, C. Lai, Y. Liu, G. M. Zeng, D. L. Huang, C. Zhang, L. Qin, L. Hu, C. Y. Zhou, W. P. Xiong, *Coord. Chem. Rev.*, **2018**, 368, 80–92.
- [30] J. T. Tang, J. L. Wang, *Chemosphere*, **2020**, 241, 125002.
- [31] V. K. Sharma, M. B. Feng, *J. Hazard. Mater.*, **2019**, 372, 3–16.
- [32] Z. H. Ye, J. A. Padilla, E. Xuriguera, E. Brillas, I. Sires, *Appl. Catal. B*, **2020**, 266, 118604.
- [33] Z. H. Ye, J. A. Padilla, E. Xuriguera, J. L. Beltran, F. Alcaide, E. Brillas, I. Sires, *Environ. Sci. Technol.*, **2020**, 54, 4664–4674.
- [34] P. K. Cao, X. Quan, K. Zhao, S. Chen, H. T. Yu, J. F. Niu, *J. Hazard. Mater.*, **2020**, 382, 121102.
- [35] P. K. Cao, K. Zhao, X. Quan, S. Chen, H. T. Yu, *Sep. Purif. Technol.*, **2020**, 248, 117022.

Graphical Abstract

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N-doped carbon-coated Fe_3N composite as heterogeneous electro-Fenton catalyst for efficient degradation of organics

Juan Xiao, Junwei Chen, Zuqiao Ou, Junhang Lai, Tongwen Yu, Yi Wang*
Sun Yat-sen University

Iron-based metal organic framework derived $\text{Fe}_3\text{N}@ \text{NG}/\text{NC}$ catalyst exhibits outstanding heterogeneous electro-Fenton performance for removing organic pollutants with good reusability and low iron leaching over a wide pH range of 3.0–9.0.

- 2020, 238, 116424.
- [36] Y. Wang, Y. H. Liu, K. Wang, S. Q. Song, P. Tsiakaras, H. Liu, *Appl. Catal. B*, **2015**, 165, 360–368.
- [37] J. Xiao, J. H. Lai, R. C. Li, X. Fang, D. F. Zhang, P. Tsiakaras, Y. Wang, *Ind. Eng. Chem. Res.*, **2020**, 59, 12431–12440.
- [38] K. Wang, H. X. Chen, X. F. Zhang, Y. X. Tong, S. Q. Song, P. Tsiakaras, Y. Wang, *Appl. Catal. B*, **2020**, 264, 118468.
- [39] J. Xiao, C. Wang, H. Liu, *J. Hazard. Mater.*, **2020**, 382, 121007.
- [40] S. Bauer, C. Serre, T. Devic, P. Horcajada, J. Marrot, G. Férey, N. Stock, *Inorg. Chem.*, **2008**, 47, 7568–7576.
- [41] H. W. Song, J. Su, C. X. Wang, *ACS Appl. Energy Mater.*, **2018**, 1, 5008–5015.
- [42] M. M. Wu, K. Wang, M. Yi, Y. X. Tong, Y. Wang, S. Q. Song, *ACS Catal.*, **2017**, 7, 6082–6088.
- [43] H. W. Song, N. Li, H. Cui, C. X. Wang, *Nano Energy*, **2014**, 4, 81–87.
- [44] X. D. Ma, X. H. Xiong, J. Q. Zeng, P. J. Zou, Z. Lin, M. L. Liu, *J. Mater. Chem. A*, **2020**, 8, 6768–6775.
- [45] T. F. Li, M. Li, M. R. Zhang, X. Li, K. H. Liu, M. Y. Zhang, X. Liu, D. M. Sun, L. Xu, Y. W. Zhang, Y. W. Tang, *Carbon*, **2019**, 153, 364–371.
- [46] P. Su, M. H. Zhou, X. Y. Lu, W. L. Yang, G. B. Ren, J. J. Cai, *Appl. Catal. B*, **2019**, 245, 583–595.
- [47] M. R. Haider, W. L. Jiang, J. L. Han, H. M. A. Sharif, Y. C. Ding, H. Y. Cheng, A. J. Wang, *Appl. Catal. B*, **2019**, 256, 117774.
- [48] Y. Q. Hua, T. T. Jiang, K. Wang, M. M. Wu, S. Q. Song, Y. Wang, P. Tsiakaras, *Appl. Catal. B*, **2016**, 194, 202–208.
- [49] J. T. Tang, J. L. Wang, *Chem. Eng. J.*, **2019**, 375, 122007.
- [50] Y. L. Yang, Y. Liu, X. Fang, W. Miao, X. Y. Chen, J. Sun, B. J. Ni, S. Mao, *Chemosphere*, **2020**, 243, 125423.
- [51] S. Cheng, C. Shen, H. Zheng, F. Q. Liu, A. Li, *Appl. Catal. B*, **2020**, 269, 118785.
- [52] J. T. Tang, J. L. Wang, *Environ. Sci. Technol.*, **2018**, 52, 5367–5377.
- [53] P. Su, M. H. Zhou, G. Song, X. D. Du, X. Y. Lu, *J. Hazard. Mater.*, **2020**, 397, 122681.
- [54] J. Y. Lu, Y. R. Yuan, X. Hu, W. J. Liu, C. X. Li, H. Q. Liu, W. W. Li, *Ind. Eng. Chem. Res.*, **2020**, 59, 1800–1808.
- [55] C. Liu, Y. Feng, Z. T. Han, Y. Sun, X. Q. Wang, Q. F. Zhang, Z. G. Zou, *Chin. J. Catal.*, **2021**, 42, 164–174.
- [56] X. Han, S. Y. Liu, X. T. Huo, F. Q. Cheng, M. Zhang, M. Guo, *J. Hazard. Mater.*, **2020**, 392, 122295.
- [57] S. Sahar, A. Zeb, Y. N. Liu, N. Ullah, A. W. Xu, *Chin. J. Catal.*, **2017**, 38, 2110–2119.
- [58] J. Wu, K. Zhu, H. Xu, W. Yan, *Chin. J. Catal.*, **2019**, 40, 917–927.
- [59] L. X. Hu, G. H. Deng, W. C. Lu, Y. S. Lu, Y. Y. Zhang, *Chin. J. Catal.*, **2017**, 38, 1360–1372.

基于N-掺杂碳包覆Fe₃N复合材料的高效异相电芬顿降解有机物

肖 娟, 陈军伟, 欧祖翘, 赖俊杭, 俞同文, 王 毅*

中山大学化学工程与技术学院, 材料科学与工程学院, 广东省低碳化学与过程节能重点实验室, 广东广州510275

摘要: 水污染导致的缺水危机、水质恶化和生态环境破坏等问题, 严重影响人的健康及社会的和谐可持续发展. 异相电芬顿技术因催化剂可循环利用、宽pH适用范围等优点而广受关注. 常见的催化剂以铁、铁氧化物等铁基材料为主, 存在金属颗粒分布不均匀、铁元素易溶出、铁循环易受阻和H₂O₂选择性和转化效率低等问题, 严重制约该技术的发展. 尽管可以通过变价金属和非金属掺杂提高H₂O₂转化效率和选择性等, 但铁基催化剂的异相电芬顿性能仍有待提升. 因此, 亟待开发一种具有合金性质且宽pH响应的高H₂O₂选择性及转化效率、高稳定性的铁基催化剂. 本文利用具有高分散的金属位点和丰富碳源的铁基金属有机骨架材料, 采用同步高温煅烧和氨气刻蚀等手段, 制备N-掺杂碳包覆Fe₃N复合材料(Fe₃N@NG/NC), 并探究了该材料在异相电芬顿降解有机污染物体系中的应用前景.

XRD, SEM和TEM测试结果表明, Fe₃N@NG/NC催化剂是由N-掺杂的石墨化碳包覆的Fe₃N纳米颗粒(大小约为70 nm)均匀分散在N-掺杂碳骨架材料中组成的, 这一特殊结构有利于电荷的快速传输, 有助于电催化氧化还原产H₂O₂及其转化至·OH反应的发生. 电化学测试结果表明, 该催化剂具有良好的两电子氧还原性能, 在电压范围为–0.3~0.1 V内的H₂O₂选择性为82.2%~74.5%, 电子转移数为2.35~2.50. 电子顺磁共振光谱结果表明, 该催化剂在异相电芬顿体系中主要的活性物质为·OH. XPS结果表明, 该催化剂中高含量的石墨N和吡啶N、Fe(II)有利于电催化合成H₂O₂和活化H₂O₂至·OH, 使其具有高效的异相电芬顿性能. 异相电芬顿降解评估结果表明, 该催化剂在pH 5.0体系中120 min内能高效去除罗丹明(RhB)、邻苯二甲酸二甲酯、亚甲基蓝和橙黄II等多种有机污染物(有机物去除率为97%~100%, TOC去除率为49%~65%), 不同RhB降解体对其去除率贡献程度依次为异相电芬顿 > 电催化 > 电生成H₂O₂氧化 > O₂氧化 > 吸附; 能实现宽pH范围内RhB的高效去除(在pH为3.0, 5.0, 7.0和9.0条件下, 在60 min内的RhB去除率分别为100%, 96%, 92%和81%); 在宽pH范围内呈现出高稳定性, 铁溶出量为0~0.03 mg/L; 经过6次循环使用后, 仍具有高的异相电芬顿性能(去除率达90%以上). 综上所述, Fe₃N@NG/NC复合材料能作为良好的异相电芬顿催化剂, 应用于污水处理领域.

关键词: Fe₃N@NG/NC复合材料; 异相电芬顿; 金属有机骨架; 降解; 有机污染物

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*通讯联系人. 电话/传真: (020)84113253; 电子邮箱: wangyi76@mail.sysu.edu.cn

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