Tailoring single-atom FeN₄ moieties as a robust heterogeneous catalyst for high-performance electro-Fenton treatment of organic pollutants

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19   **Abstract**

20   An iron single-atom catalyst, composed of robust FeN_4 moieties anchored on a nitrogen-

21   doped porous carbon matrix (Fe-SAC/NC), has been developed via a surfactant-

22   coordinated metal-organic framework (MOF) approach for application in heterogeneous

23   electro-Fenton (HEF) process. The cohesive interaction between the surfactant and MOF

24   precursor enabled the formation of abundant and stable FeN_4 moieties. The Fe-SAC/NC-

25   catalyzed HEF allowed the complete degradation of 2,4-dichlorophenol with low iron

26   leaching (1.2 mg L^{-1}), being superior to nanoparticle catalyst synthesized without

27   surfactant. The experiments and density functional theory (DFT) calculations

28   demonstrated the dominant role of single-atom FeN_4 sites to activate the electrogenerated

29   H_2O_2 yielding $^{\bullet}OH$. The dense FeN_4 moieties allowed harnessing the modulated

30   electronic structure of the SAC to facilitate the electron transfer, whereas the adjacent

31   pyrrolic N enhanced the adsorption of target organic pollutants. Moreover, the excellent

32   catalysis, recyclability and viability of the Fe-SAC/NC were verified by treating several

33   organic pollutants even in urban wastewater.

34   *Keywords*: Advanced oxidation process; Electro-Fenton; Metal-organic framework;

35   Single-atom catalyst; Water treatment

36

1. Introduction

As a result of the booming demand of healthcare products (e.g., pharmaceuticals), crop protection products (e.g., pesticides) and a myriad of synthetic industrial goods, refractory organic micropollutants, some of which act as endocrine disrupting chemicals (EDCs), are frequently present in water bodies and eventually jeopardize living beings health and ecosystems [1-4]. In the last decade, the electro-Fenton (EF) process has been demonstrated to be highly effective and eco-friendly alike for the treatment of such pollutants in wastewater [5,6]. The EF setups rely on the electrogeneration of H_2O_2 at carbonaceous cathodes, which occurs with great faradaic efficiency from O_2 reduction reaction. This in-situ reaction allows minimizing the dangers, hazards and costs associated to industrial H_2O_2 synthesis [7-9]. The accumulated H_2O_2 is immediately decomposed in the presence of Fe(II) catalyst, yielding abundant active hydroxyl radicals ($^\bullet$OH) in the bulk solution via Fenton's reaction [6]. Nonetheless, the large-scale application of homogeneous EF (i.e., process in which free iron ions are used as catalyst) is limited by the requirement of strict acidic pH and the gradual conversion of dissolved iron into precipitate (mud) [10,11]. Lately, a strategy based in the use of solid iron-rich materials as heterogeneous EF catalysts has gained momentum to minimize these disadvantages, although new concerns have emerged in parallel [12]. The polyatomic nature of the catalysts limits the exposure of iron active sites to H_2O_2, which must be adsorbed prior to activation, and the relatively poor electron transfer between the reactants (especially the restrained Fe(III)/Fe(II) redox cycling) is detrimental to the overall catalytic performance [6,13]. Furthermore, the progressive deactivation and/or loss of active iron sites affects the catalyst stability and durability, ending in nonviable materials in practice [14,15]. It is thus evident that progress in design of catalysts with well-balanced performance and stability is of major importance.

62   At present, the development of strong Fe-N ensembles embedded in carbon matrices

63   (denoted as Fe-N-C) is considered to be a promising strategy for the improvement of

64   activity, stability and reusability of the iron-based catalysts [16,17]. N-doping contributes

65   to the modulation of charge distribution of sp^2-hybridized carbon framework and creates

66   new defects [18,19]. The electron-rich N sites coordinate with Fe atoms to form the so-

67   called FeN_x moieties [20], which exhibit fast electron transfer ability and are considered

68   as the actual active centers in many catalytic processes [21,22]. Moreover, the strong

69   binding between Fe and N atoms confers a greater stability to the metal active sites and

70   hence, to the whole catalyst during the given process [23]. As an example, Hu et al.

71   fabricated an iron-based catalyst with core-shell structure and abundant Fe_3C and FeN_x

72   sites; in an HEF system, the Fe_3C sites played a key role for H_2O_2 generation and FeN_x

73   promoted the H_2O_2 activation [13]. Other studies have revealed the role of various N-

74   functionalities present in the catalysts during the treatment of organic pollutants by

75   Fenton-based processes; pyrrolic N facilitates the adsorption of pollutants through π-π

76   and/or cation-π interactions, whereas N-doping eases the electron transfer through both

77   the external circuit and the carbon framework to enhance the Fe(III) reduction [8,9,24,25].

78   As a result, the electronic configuration of the π-conjugated ligands linked to FeN_4 sites

79   is relocated, which alters the rate-determining steps of the given reaction. In this regard,

80   FeN_4 sites have been proven superior as compared to other coordination geometries

81   (FeN_1, FeN_2 and FeN_3) [26]. Unfortunately, for most Fe-N-C catalysts synthesized via

82   conventional pyrolysis routes, a large proportion of FeN_x moieties are hidden and

83   inaccessible to the reactants during the EF process, and the lack of strategies to precisely

84   modulate the coordination number in FeN_x moieties limits the overall activity.

85   Single-atom catalysts (SACs), with individual metal sites atomically dispersed on the

86   substrate, constitute a new frontier in catalysis. They have shown superior catalytic

4

87   performance as well as higher selectivity and stability in many research fields due to their

88   outstanding characteristics: unsaturated coordination configurations, fully exposed active

89   sites, strong metal-substrate interactions and quantum size effects [17,27-29]. The

90   application of Fe-SACs in advanced oxidation processes has become a very relevant

91   topic, as can be deduced from recent works: Chen and co-workers prepared Fe-SAC

92   anchored nitrogen-rich g-C_3N_4 nanotubes for peracetic acid activation by Fenton-like

93   reaction [30]; Xiong and co-workers fabricated an Fe-SAC using Fe(phen)$_3$ and SBA-15

94   as the precursors for peroxymonosulfate activation [31]; several authors reported the

95   application of Fe-SACs in HEF, trying to tune the multi-electron oxygen reduction

96   process to enable the O_2-to-$^\bullet$OH conversion [32-34]. Unfortunately, few studies address

97   the rational design of dense single-atom FeN_4 sites for water treatment by HEF process,

98   and the synthesis of SACs still remains challenging due to the easy aggregation of metal

99   atoms [35,36].

100   Metal-organic frameworks (MOFs), as ultraporous materials formed by the spatial

101   assembly of metal nodes and organic linkers, are common precursors to fabricate Fe-

102   SACs due to the large number of metal sites, ordered pores, large exposed surface and

103   diverse chemistry that is offered upon small structural changes [12,37,38]. Additionally,

104   nitrogen atoms from the organic linkers can promote the anchorage of the highly mobile

105   iron atoms, giving rise to strong FeN_x configurations [37,39-41]. Despite this, the

106   methodology still suffers from considerable aggregation of iron atoms because of the

107   carbon loss at high temperature [42]. This article addresses, for the first time, the rational

108   design of an Fe-SAC with robust FeN_4 moieties (Fe-SAC/NC) by the pyrolysis of a

109   surfactant-coordinated MOF, followed by the application to boost HEF treatment of

110   organic micropollutants in both model solution and urban wastewater. The involved

111   surfactant, cetyltrimethylammonium bromide, was able to regulate the crystallization of

112 the MOF precursor, coordinating with the surface metal sites to form a surfactant shell.

113 During the pyrolysis, the CTAB layers were decomposed into an N-doped carbon shell,

114 which acted as additional carbon and nitrogen source to stabilize the iron single-atom

115 sites and mitigate their agglomeration. Some density functional theory (DFT) calculations

116 are also included in this study, trying to elucidate the role of the single-atom FeN_4 sites.

117 **2. Materials and methods**

118 **2.1 Catalysts synthesis**

119   The synthesis route of Fe-SAC/NC is schematized in Fig. 1a. In brief, 1.00 g of

120 CTAB, 2.38 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 1.10 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 50 mL

121 methanol to form a clear solution. Then, 50 mL of methanol containing 3.63 g of 2-

122 methylimidazole were injected into the above mixture. After stirring for 30 min at 60 °C,

123 the resulting precipitate was centrifuged, sequentially cleaned with ethanol for several

124 times, and finally dried at 60 °C for 12 h. The resulting MOF was transferred into a tube

125 furnace to be heated at 900 °C for 3 h under nitrogen atmosphere. The carbonization

126 product was treated with 0.2 M HCl solution for 2 h at 50 °C, then cleaned with ethanol

127 and dried overnight. The final catalyst is denoted as Fe-SAC/NC or Fe1/2Zn-1.0CTAB.

128 The preparation of catalysts with different CTAB dosage (0, 0.1, 0.5 and 1.5 g) followed

129 a similar procedure, and the obtained catalysts are denoted as Fe1/2Zn-0CTAB (the

130 absence of surfactant gives rise to nanoparticle catalyst, Fe-NP/NC), Fe1/2Zn-0.1CTAB,

131 Fe1/2Zn-0.5CTAB and Fe1/2Zn-1.5CTAB, respectively.

132 **2.2 Evaluation of catalytic performance**

133   The electrolytic assays were carried out in a single chamber glass cell that contained

134 160 mL of solution to be treated at room temperature. The cell was equipped with a gas-

135 diffusion electrode (GDE, 3 cm^2) as cathode, with air supplied at 1 L min^{-1} for constant

136   H_2O_2 production on site, and a Ti|IrO$_2$-based dimensionally stable plate (DSA, 3 cm^2) or

137   a boron-doped diamond thin film (Si|BDD, 3 cm^2) as the anode. The gap between the

138   anode and cathode was 1.0 cm. Constant current was applied using a DC power supply

139   (IT6302 from ITECH, China). The EF treatments were performed after catalyst addition.

140   Samples were obtained at selected times and immediately filtered with PTFE syringe

141   filters (0.22 μm) to remove particles. The degradation performance was evaluated by

142   measuring the concentration of pollutants using reversed-phase high performance liquid

143   chromatography (HPLC, SCION6000, China), as described in Supplementary Material

144   (SM).

145   **2.3 Characterization and Analytical Procedures**

146   Several techniques, including X-ray absorption near edge structure (XANES) and

147   extended X-ray absorption fine structure (EXAFS), high-resolution transmission electron

148   microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction

149   (XRD), thermogravimetric analysis (TGA), Raman analysis and inductively coupled

150   plasma (ICP) were employed to analyze the morphology, chemical and electronic

151   structures, and other properties of the synthesized materials. The details are given in SM.

152   The analytical methods for determination of pH, H_2O_2 and dissolved iron concentrations,

153   and total organic carbon (TOC) are also explained in SM.

154   **2.4 Computational Details**

155   Structural modelling and DFT calculations were carried out employing the Materials

156   Studio software package. The exchange-correlation interaction was described by

157   generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)

158   functional. The Brillouin zone was sampled by a Monkhorst-Pack $2 \times 2 \times 1$ K-point grid.

159   The lattice constants were calculated using lattice parameters of 14.726 Å $\times$ 12.7825 Å $\times$

160   15.000 Å. The vacuum slab was set up to 15 Å. The geometric optimization was

161   terminated when the energy and force on each ion dropped below 10^{-5} Ha (3×10^{-4} eV)

162   and 0.002 Ha $Å^{-1}$ (0.05eV $Å^{-1}$).

3. Results and discussion

3.1 Characterization of the MOF-derived catalyst

165   Fe-SAC/NC was prepared by carbonization of surfactant-coordinated Fe/ZIF-8

166   precursor at 900 °C under N_2 atmosphere (Fig. 1a). The surface Fe/Zn metal nodes in

167   ZIF-8 crystals can coordinate with the hydrophilic groups of CTAB to form surfactant

168   shells. The coordination-driven self-assembly slows down the crystal growth rate and

169   controls the shape and size of ZIF-8 crystals. During the pyrolysis, the surfactant layers

170   were the first ones to decompose at temperature from around 330 °C (Fig. S1), forming

171   ultrathin carbon layers at the surface. Finally, the zinc metal nodes were volatilized at

172   high temperature (boiling point at 907 °C), leaving atomically-anchored Fe on the N-

173   doped porous carbon matrices. Worth remarking, the cohesive interaction between CTAB

174   and MOF crystals allowed a confinement effect that suppressed the agglomeration of Fe

175   atoms, eventually yielding a large amount of atomically dispersed FeN_4 active sites.

176   Moreover, the N groups in CTAB provide additional N source to enhance the

177   coordination between Fe and N [43]. The TEM images depicted in Fig. 1b-d also confirm

178   the distinct carbon layer coating on the surface, and the catalyst partially inherited the

179   morphology of the MOF precursor, which may enhance the stability and the mass

180   transport during the reaction. The XRD patterns of Fe-SAC/NC and ZIF-8-derived N-

181   doped carbon matrices, as shown in Fig. 2a, exhibited only two peaks centered at 24.3°

182   and 44.5°, which were assigned to (002) and (004) crystal planes of carbon, respectively

183   [44,45]. No diffraction peak related to Fe-based species (iron oxides, iron nitrides or iron

184   carbides) appeared, evidencing that Fe sites were atomically dispersed in Fe-SAC/NC. In

185   contrast, a high amount of Fe atoms in the Fe-NP/NC, prepared in the absence of CTAB,

186   existed in the diffractogram of Fe_3N (Fig. 2b) [46].

187   Further evaluation of the coordination state and electronic features of Fe-SAC/NC is

188   crucial for in-depth understanding of the catalytic mechanisms underlying in the HEF

189   system. First, the XPS analysis was performed to reveal the chemical compositions and

190   the corresponding electronic states of the catalyst. The high resolution Fe $2p$ spectra of

191   Fe-NP/NC and Fe-SAC/NC (Fig. 2c) illustrate two splitting peaks at binding energies of

192   710.80 and 713.41 eV for the former material, which could be attributed to Fe(II) and

193   Fe(III) species, respectively [47,48]. However, both peaks in Fe-SAC/NC slightly shifted

194   to lower binding positions (710.16 and 712.77 eV), whereas the peak area of Fe(II)

195   increased to 63.3% compared to the 58.1% in Fe-NP/NC. These results are ascribed to

196   the introduction of CTAB, which enhances the dispersion of Fe atoms and the formation

197   of FeN_x moieties during the pyrolysis. Nitrogen from CTAB can bond with iron atoms

198   and decrease their electron density, thus enhancing the Fe(III) to Fe(II) conversion by

199   accelerating the electron transfer from carbon to iron sites [49,50]. Meanwhile, the

200   increase in the amount of carbon in Fe-SAC/NC (Fig. S2) further facilitated the

201   stabilization and reduction of Fe(III) atoms. Additionally, the Fe loading in Fe-SAC/NC

202   was measured by ICP as 8.5 wt%. In N $1s$ spectra (Fig. 2d), graphitic N (401.3 eV),

203   pyrrolic N (400.3 eV), Fe-N (399.7 eV), and pyridinic N (398.9 eV) were observed in

204   both samples [21,51-54]. Worth noting, the proportion of pyrrolic N was higher and Fe-

205   N was lower in Fe-SAC/NC as compared to Fe-NP/NC. As reported, Fe-N sites usually

206   act as the catalytic centers for the activation of H_2O_2 to form $^\bullet OH$, and pyrrolic N can

207   serve as adsorption sites for target pollutants during the wastewater treatment [13,55,56].

208   Therefore, higher amount of pyrrolic N and Fe-N may give rise to better catalytic

209   performance of the catalysts. In addition, the proportion of pyrrolic N and Fe-N was

210   greater with the increase of CTAB dosage during the synthesis, but excessive CTAB (i.e.,

211   1.5 g) led to the decrease in the proportion of pyrrolic N (Fig. 2e).

212   Further analysis of the surface defect states of Fe1/2Zn-1.0CTAB and Fe1/2Zn-

213   1.5CTAB was conducted by Raman spectroscopy. In Fig. 2f, two distinct peaks are

214   observed at 1350 cm^{-1} and 1600 cm^{-1}, which are assigned to defective D and graphitic G

215   bands, respectively. These two peaks can be further deconvoluted into four peaks through

216   Gaussian numerical simulation, namely the sp^2-type (at ~1350 cm^{-1} and ~1600 cm^{-1}) and

217   the sp^3-type carbon (at ~1200 cm^{-1} and ~1500 cm^{-1}). And the integrated area ratio of sp^3-

218   type/sp^2-type carbon (A$_{sp3}$/A$_{sp2}$) enables the evaluation of the relative contents of

219   defective and graphitic carbon [57]. The I$_D$/I$_G$ value, referring to the intensity ratio of the

220   D-band to G-band, was approximately 1.30 and 1.08 for Fe1/2Zn-1.0CTAB and Fe1/2Zn-

221   1.5CTAB, respectively, suggesting the formation of more lattice defects in the N-doped

222   porous carbon matrices of Fe1/2Zn-1.0CTAB. In addition, the A$_{sp3}$/A$_{sp2}$ value for

223   Fe1/2Zn-1.0CTAB was as low as 0.38, which further demonstrates the high defective

224   degree and outstanding electronic conductivity [58,59]. As reported, the catalysts with

225   abundant defects are endowed with localized electrons, and the accelerated electron

226   transfer facilitates the dissociation of H$_2$O$_2$ to •OH and Fe(III)/Fe(II) redox cycling [60-

227   62].

228   The chemical states and local coordination environment of Fe atoms in Fe-SAC/NC

229   were investigated by XANES and EXAFS. Fig. 3a displays the normalized Fe K-edge

230   XANES spectra of the as-synthesized Fe-SAC/NC and the corresponding Fe foil, FeO

231   and Fe$_2$O$_3$ references. The increase in the valence of Fe would lead to the migration of the

232   rising edge to higher energy region [23]. As can be seen, the near-edge absorption energy

233   of the Fe K-edge for Fe-SAC/NC located between those of FeO and Fe$_2$O$_3$, indicating

234   that the Fe atoms in the sample carried a positive charge with the oxidation value between

+2 and +3. The Fourier transform extended X-ray absorption fine structure (FT-EXAFS) spectrum of Fe-SAC/NC in Fig. 3b exhibits a prominent peak at ~1.6 Å, which can be assigned to Fe-N bonds [63]. The typical peak for Fe-Fe scattering path, located at ~2.4 Å in the Fe foil, is absent in the spectrum of Fe-SAC/NC, providing solid evidence for the absence of metallic iron clusters or nanoparticles in the sample. The EXAFS fitting analysis further revealed the coordination environment of Fe in Fe-SAC/NC. The fitting results in Fig. 3c and Table S2 verified that each Fe atom was coordinated by 4 N atoms with the mean bond length of ~2.07 Å. Moreover, the EXAFS wavelet transform (WT) plot of Fe-SAC/NC (Fig. 3d) only displayed an intensity maximum at 5.0 Å that is associated with the Fe-N coordination, being clearly distinguished from the Fe-Fe connection at 8.3 Å depicted in the plot of Fe foil. According to these results, it can be concluded that the Fe-SAC/NC with robust single-atom FeN_4 sites was successfully fabricated.

3.2 Evaluation of the catalytic activity of Fe-SAC/NC

To estimate the catalytic activity of the Fe-SAC/NC as a potential HEF catalyst, 2,4-dichlorophenol (2,4-DCP) was selected as the target contaminant to be treated by different processes (Fig. 4a). In electrochemical oxidation with in-situ generation of H_2O_2 at the cathode (so-called EO-H_2O_2) [64], only a small 2,4-DCP removal of 17.3% in 90 min was achieved. The adsorption efficiency of 2,4-DCP by Fe-SAC/NC was also as low as 15.6%. These results suggest the negligible contribution of anodic oxidation and adsorption to 2,4-DCP removal. In contrast, complete abatement of 2,4-DCP was reached by Fe-SAC/NC-catalyzed HEF process in 90 min, with extremely low iron leaching (1.23 mg L^{-1}), behaving much better than HEF with Fe-NP/NC catalyst that only allowed attaining a 40.9% removal. The remarkable catalytic activity and stability of the Fe-SAC/NC can be ascribed to the abundant accessible single-atom FeN_4 sites.

260　　　　Since the chemical states and electronic features of the catalysts may vary under

261　　different synthesis conditions, the catalysts prepared with different amount of CTAB

262　　source were tested in the HEF treatment of 2,4-DCP. As depicted in Fig. 4b, Fe1/2Zn-

263　　1.0CTAB exhibited the best activity in terms of 2,4-DCP degradation, attaining a 99.3%

264　　removal at 60 min, being superior to Fe1/2Zn-1.5CTAB (95.3%), Fe1/2Zn-0.5CTAB

265　　(60.9%) and Fe1/2Zn-0.1CTAB (47.1%). As described in Fig. S3, the proportion of

266　　different N species in the catalyst highly depended on the dosage of CTAB and, among

267　　them, Fe-N and pyrrolic N may play significant roles in the removal of 2,4-DCP.

268　　Therefore, the relationship between the kinetic constants for the degradation of 2,4-DCP

269　　and the relative contents of Fe-N and pyrrolic N in the catalysts can be inferred from data

270　　shown in Fig. 4c and Fig. 2e, respectively. The increase in the CTAB dose from 0.1 to 1.0

271　　g led to growing percentages of Fe-N and pyrrolic N, which also yielded quicker 2,4-DCP

272　　disappearance. The results verify again the positive effect of Fe-N and pyrrolic N on the

273　　catalytic performance. However, further increase of the CTAB dosage to 1.5 g was

274　　detrimental, evidenced from the less effective 2,4-DCP abatement. This was due to the

275　　fact that excessive CTAB hinders the nucleation and growth of ZIF-8 precursor, then

276　　hampering the formation of single-atom FeN_4 sites despite the increase in the Fe-N

277　　content.

278　　　　The effect of various operation parameters, including pH, catalyst dosage and applied

279　　current, on the 2,4-DCP concentration decay upon the application of Fe-SAC/NC-

280　　catalyzed HEF treatment was explored. As expected, increasing the catalyst dosage from

281　　0.05 to 0.20 g L^{-1} allowed the substantial enhancement of 2,4-DCP concentration decay

282　　(Fig. 4d). Notably, a dramatic increase in the 2,4-DCP removal was achieved when the

283　　catalyst dosage was increased from 0.05 to 0.10 g L^{-1}, with only a small rise in iron

284　　leaching (i.e., 0.26 mg L^{-1}, see inset), indicating that the greater catalytic performance

285   was due to the increased amount of single-atom FeN_4 active sites rather than the

286   homogeneous Fenton's reaction by the dissolved iron ions. As shown in Fig. 4e, the

287   quickest decay of 2,4-DCP was observed at initial pH 3.0, and the degradation efficiency

288   was gradually decreased with the increase in pH value. The enhanced performance at

289   more acidic pH is logically attributed to the higher oxidation potential of $^\bullet OH$ at low pH,

290   as well as the contribution of homogeneous Fenton's reaction occurring from dissolved

291   iron ions (Fig. 4f). In other words, the loss of atomically dispersed iron sites at strong

292   acidic pH would reduce the recyclability of Fe-SAC/NC. Fortunately, 100% and 96.8 %

293   2,4-DCP removal could be still obtained at initial pH 4.0 and 5.0 with low iron leaching

294   of 1.23 and 0.96 mg L^{-1}, respectively, corroborating both the high activity and stability of

295   the catalyst at near-neutral pH. Fig. S4 illustrates the positive effect of applied current

296   increase on pollutant removal. The higher current gave rise to greater H_2O_2 accumulation

297   in the bulk and, consequently, to a higher amount of $^\bullet OH$. The catalytic performance of

298   Fe-SAC/NC-based HEF system was further investigated by treating several organic

299   pollutants separately. As illustrated in Fig. 5a, the complete degradation of Rhodamine B,

300   trimethylolpropane and ciprofloxacin and more than 90% removal of Methyl Orange can

301   be observed in 30 min, whereas other pollutants were also completely removed in 60 min.

302   Such results can be explained by the unique feature of $^\bullet OH$, being nonselective in the

303   degradation of most organics. Besides, the physicochemical properties of the organics,

304   such as molecular structure and electron affinity, can affect their adsorption and

305   decomposition, leading to different kinetic constants (Fig. 5a).

306   **3.3 Recyclability and applicability of Fe-SAC/NC**

307   Apart from the catalytic activity, the recyclability of the Fe-SAC/NC was also

308   assessed from cycling tests. As depicted in Fig. 5b, the complete removal profiles of 2,4-

309   DCP remained unaltered after five successive runs, demonstrating the remarkable

310 recyclability of Fe-SAC/NC. The leached iron concentration was 1.23 mg L^{-1} at the first

311 cycle, then being undetectable after the second run. The slight decrease in the degradation

312 kinetic constant, especially in the fourth and fifth runs, informs about certain deactivation

313 of catalyst due to the loss of FeN$_4$ active sites and the adsorption of some organic

314 intermediates on the surface during the long-term operation. The optimization of the

315 cleaning procedure based on organic solvent and weak acid solution may increase its

316 regeneration.

317 The applicability of Fe-SAC/NC in real cases was further evaluated by treating 2,4-

318 DCP in urban wastewater at initial pH 4.0 (Fig. 5c). The almost total disappearance of

319 2,4-DCP at 90 min is evidenced, being the removal slower than that in simulated aqueous

320 matrix due to the competition of other organics in wastewater for the $^{\bullet}$OH [56]. Moreover,

321 the mineralization ability of Fe-SAC/NC-catalyzed HEF process was assessed from TOC

322 analysis. In Fig. 5d, it can be seen that the BDD/air-diffusion cell achieved a substantial

323 mineralization of 67.6% at 300 min, outperforming that with a RuO$_2$-based DSA anode

324 thanks to the production of physisorbed BDD($^{\bullet}$OH) [65]. Consequently, the Fe-SAC/NC-

325 catalyzed HEF system owns an interesting recyclability and applicability.

326 **3.4 Mechanistic Insights**

327 The electrochemical impedance spectroscopy (EIS) Nyquist plots were obtained to

328 evaluate the ability of the Fe-SAC/NC to shuttle and conduct the surface charge (Fig. S5).

329 The R_{ct} value (inset), which is related to the charge-transfer resistance of the catalyst, was

330 acquired from the fitting of the corresponding equivalent circuit [66,67]. The results in

331 Fig. S5 revealed that the R_{ct} values for Fe-SAC/CN and Fe-NP/CN were 3.44 and 7.10

332 kΩ, respectively, demonstrating the enhanced charge transfer efficiency of Fe-SAC/NC

333 due to the addition of CTAB during the synthesis.

DFT calculations on the Gibbs free energy during H_2O_2 adsorption and activation by the FeN_4 or Fe_3N sites were carried out comparatively to provide insights into the catalytic mechanisms. The details are shown in Fig. 6a. The H_2O_2 molecule is first adsorbed on the top of the iron site (FeN_4 or Fe_3N) with one of the O atoms bound to the iron atom (H_2O_2*). The $HOO-FeN_4$ or $HOO-Fe_3N$ bond (HOO*) is then achieved by releasing one proton. Finally, the O-O bond of the intermediate HOO* is broken to yield the HO* species, which can be desorbed from the catalyst quickly to degrade the organic molecules [59,68,69]. The superior catalytic activity of Fe-SA/NC over Fe-NP/NC for HEF can be ascribed to two facts: (i) the desorption step to yield •OH species in Fe-SAC/NC is an exothermal reaction and a feasible process, whereas the formation of the same oxidant from $HO-FeN_4$ bond is an endothermal reaction (Fig. 6, right plot); (ii) the Gibbs free energy difference value of Fe-SAC/NC (ΔG = -3.110 eV) is greater than that of Fe-NP/NC (ΔG = -2.758 eV) during the breakage of HOO* to HO*, indicating the easier cleavage of H_2O_2 to form •OH. Such differences confirm the excellent activity of single-atom FeN_4 sites towards H_2O_2 activation, in full agreement with the previous experimental results.

Based on the above findings, a detailed mechanism explaining the superior performance of Fe-SAC/NC-catalyzed HEF treatment of 2,4-DCP (also valid for other organic pollutants) is proposed (Fig. 7). First, the in-situ generated H_2O_2 at the cathode can be efficiently adsorbed at the FeN_4 sites; then, it is rapidly decomposed to form a large number of •OH via the interaction between H_2O_2 and FeN_4 sites. Meanwhile, the pyrrolic N in the catalyst favors the adsorption of the pollutant through the π-π and/or cation-π interactions. The enhanced mass transport decreases the migration distance between •OH and target 2,4-DCP molecules, resulting in the efficient degradation of the pollutant. As the reactions proceed, the single-atom FeN_4 sites undergo repetitive interconversion of the states during H_2O_2 adsorption and activation, leading to excellent

359 catalytic performance. On the other hand, the ultrathin carbon layer derived from CTAB

360 not only suppresses the agglomeration of iron atoms, but also facilitates the formation of

361 robust FeN_4 moieties during the synthesis. The coordination between Fe and N actually

362 decreases the electron density of iron sites due to the high electronegativity of N element,

363 which accelerates the Fe(III)/Fe(II) redox cycling during the treatment.

364 **4. Conclusions**

365   Robust single-atom FeN_4 sites anchored on an N-doped carbon matrix were

366 successfully prepared for the efficient HEF treatment of 2,4-DCP and other organic

367 pollutants. Complete abatement of 2,4-DCP was attained by Fe-SAC/NC-catalyzed HEF

368 process at 90 min, with very low iron leaching (1.23 mg L^{-1}), which was superior to HEF

369 with Fe-NP/NC catalyst that only allowed 41% 2,4-DCP removal. The Fe-SAC/NC

370 exhibited reasonable stability and recyclability in HEF system. The dominant role of FeN_4

371 sites was verified from the thorough catalyst characterization and the experimental assays

372 and DFT calculations. The modulation of the electronic structure of the catalyst by

373 constructing dense FeN_4 moieties facilitated the electron transfer to yield a larger amount

374 of $^{\bullet}$OH during the HEF, whereas the adjacent pyrrolic N enhanced the adsorption of target

375 organic pollutants. These findings provide new insights into the rational design of highly

376 active, stable, and multi-functional HEF catalysts, and inspire the exploration and

377 application of electrochemical advanced oxidation technologies for real wastewater

378 treatment.

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1 **Figure captions**

2 **Fig. 1.** (a) Scheme of the preparation method of the Fe-SAC/NC, ending in a

3 representation of the atomic network. (b-d) TEM images of the obtained Fe-SAC/NC, at

4 different magnifications.

5 **Fig. 2.** XRD patterns of (a) Fe-SAC/NC and ZIF-8-derived NC and (b) Fe-NP/NC. High

6 resolution (c) Fe $2p$ and (d) N $1s$ XPS spectra of Fe-NP/NC (prepared with 0 g CTAB)

7 and Fe-SAC/NC (prepared with 1.0 g CTAB). (e) The pyrrolic N and Fe-N percentages

8 in the catalysts with the CTAB content employed during the synthesis. (f) Raman spectra

9 of Fe1/2Zn-1.0CTAB and Fe1/2Zn-1.5CTAB.

10 **Fig. 3.** (a) XANES curves and (b) FT-EXAFS curves at Fe K-edge obtained for Fe foil,

11 FeO, Fe_2O_3, and Fe-SAC/NC. (c) Corresponding fitting for the FT-EXAFS curve of Fe-

12 SAC/NC over the R space range (inset: model of FeN_4 site in Fe-SAC/NC; the red, pink,

13 and blue balls represent Fe, N and C, respectively). (d) Wavelet transform (WT) contour

14 plots of Fe K-edge for Fe foil, FeO, Fe_2O_3 and Fe-SAC/NC.

15 **Fig. 4.** (a) Normalized 2,4-DCP concentration decay during different treatments of 160

16 mL of 0.14 mM 2,4-DCP solutions with 0.05 M Na_2SO_4. (b) Effect of CTAB dosage,

17 employed during the catalyst preparation, on the catalytic performance during the HEF

18 treatment of 2,4-DCP solutions (inset: the corresponding kinetic analysis and pseudo-

19 first-order rate constants). (c) Dependence of the rate constant values (k_{obs}) for 2,4-DCP

20 degradation (extracted from Fig. 4b). Effect of (d) catalyst dosage and (e) initial pH on

21 the time course of normalized 2,4-DCP concentration during the Fe-SAC/NC-catalyzed

22 HEF treatment (inset in (d): iron concentration after 90 min treatment). (f) Iron

23 concentration and final pH after 90 min of the electrolytic trials shown in Fig. 4e.

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Fig. 5. (a) The degradation performance of Fe-SAC/NC-catalyzed HEF process considering different target organic pollutants, e.g., naproxen (NPX), 2,4-DCP, trimethylolpropane (TMP), ciprofloxacin (CIP), Methyl Orange (MO), and Rhodamine B (RhB). (b) Recycling of Fe-SAC/NC in the HEF treatment of 2,4-DCP solutions. (Unless otherwise stated, the parameters in each figure are: TOC of 10 mg L^{-1} C; [Catalyst] = 0.10 g L^{-1}; initial pH = 4.0; applied current = 50 mA). (c) Degradation of 2,4-DCP in 160 mL of urban wastewater by Fe-SAC/NC-catalyzed HEF process at pH 4.0 and applied current of 50 mA. (d) Change of normalized TOC with reaction time during HEF treatment of 2,4-DCP solutions using a DSA or BDD anode under the conditions of the trial shown in Fig. 4a.

Fig. 6. Reaction pathways for H_2O_2 adsorption and activation at FeN_4 and Fe_3N sites, and required energy calculated by DFT.

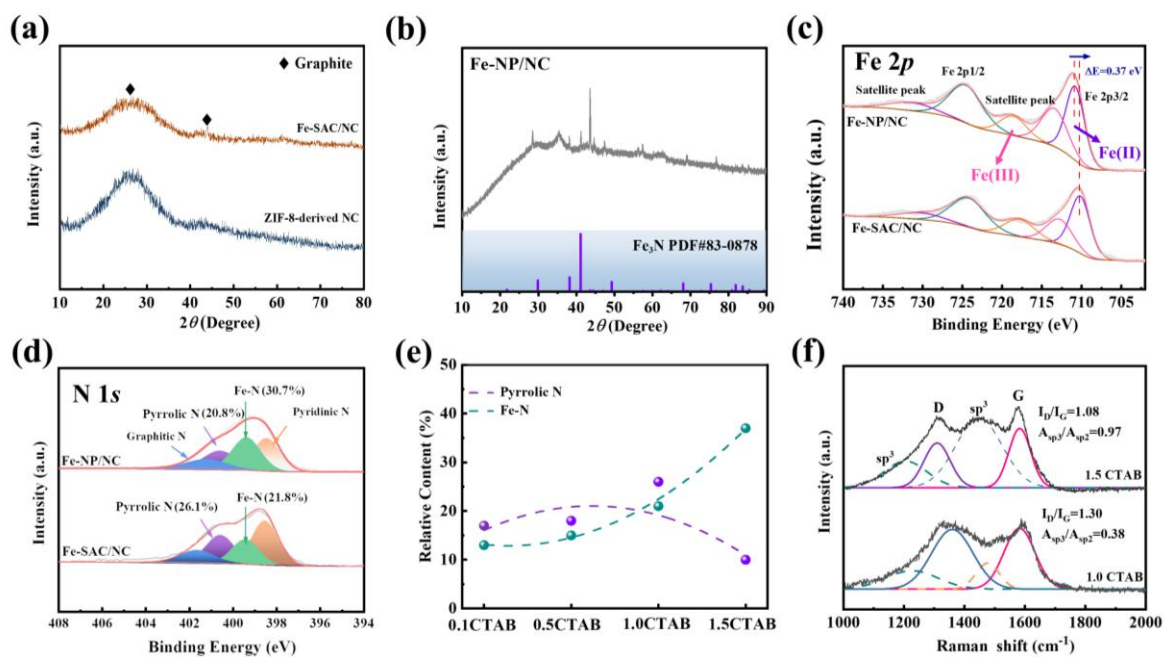**Fig. 7.** Proposed mechanism for Fe-SAC/NC-catalyzed HEF degradation of 2,4-DCP.

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Fig. 1

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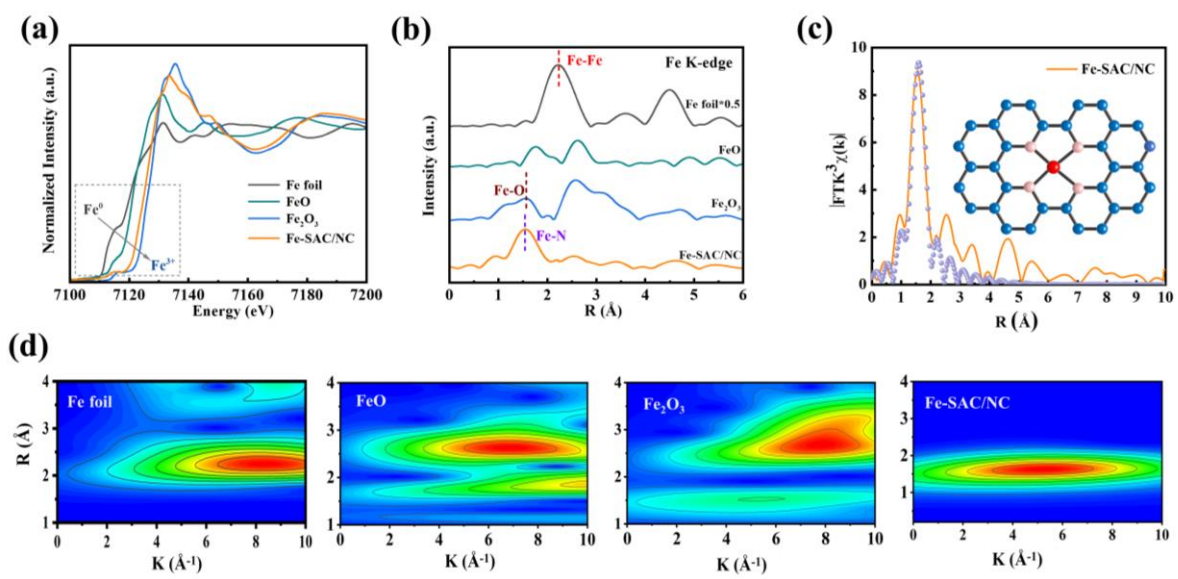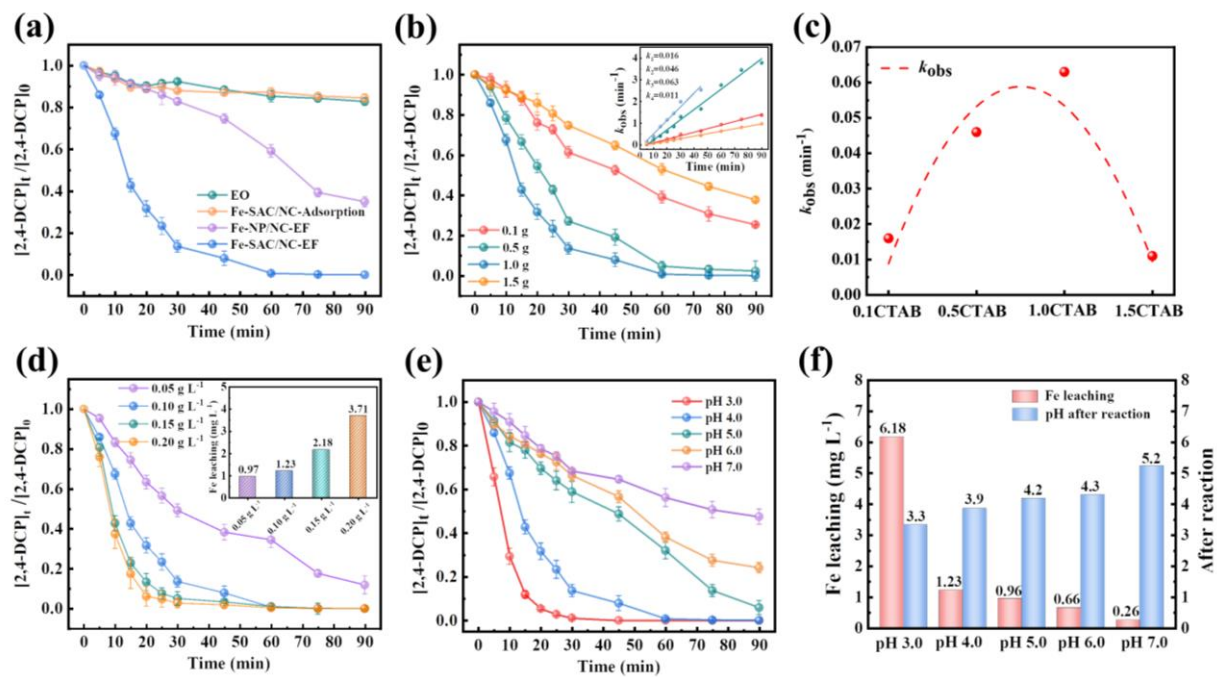44

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Fig. 2

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Fig. 3

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Fig. 4

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Fig. 5

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71   **Fig. 6**

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Legend:
● 2,4-DCP   ● 2,4-DCP degradation byproducts

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76   **Fig. 7**