Enhanced Perfluorooctanoic Acid Degradation by Electrochemical Activation of Sulfate Solution on B/N Codoped Diamond

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ABSTRACT: Electrochemical oxidation based on SO4** and *OH generated from sulfate electrolyte is a cost-effective method for degradation of persistent organic pollutants (POPs). However, sulfate activation remains a great challenge due to lack of active and robust electrodes. Herein, a B/N codoped diamond (BND) electrode is designed for electrochemical degradation of POPs via sulfate activation. It is efficient and stable for perfluorooctanoic acid (PFOA) oxidation with first-order kinetic constants of 2.4 h⁻¹ and total organic carbon removal efficiency of 77.4% (3 h) at relatively low current density of 4 mA cm⁻². The good activity of BND mainly originates from a B and N co-doping effect. The PFOA oxidation rate at sulfate electrolyte is significantly enhanced (2.3–3.4 times) compared with those at nitrate and perchlorate electrolytes. At sulfate, PFOA oxidation rate decreases slightly in the presence of *OH quencher while it declines significantly with SO4** and *OH quenchers, indicating both SO4** and *OH contribute to PFOA oxidation but SO4** contribution is more significant. On the basis of intermediates analysis, a proposed mechanism for PFOA degradation is that PFOA is oxidized to shorter chain perfluorocarboxylic acids gradually by SO4** and *OH until it is mineralized.

INTRODUCTION

Persistent organic pollutants (POPs) are globally distributed in the environment in increasing amounts. They are refractory, highly toxic, and bioaccumulative, which have caused environmental and human health concerns. POPs such as perfluorooctanoic acid (PFOA) are difficult to degrade by most conventional methods and are frequently detected in the environment. Developing efficient methods to degrade these contaminants is urgently needed. Electrochemical oxidation has attracted increasing interest in water treatment due to its mild and reagent free conditions.1,2 It can be powered by solar electricity, which makes it promising and sustainable.

Indirect electrochemical oxidation through reactive specialists (*OH, SO4**, O₂, ClO⁻ etc.) generated on anode is a preferable pathway for POPs degradation as it is usually more efficient than direct oxidation.3-6 SO4** and *OH radicals have strong oxidation ability toward a broad spectrum of refractory organic pollutants (E°(SO4**/SO4⁻) = 2.5–3.1 V, E°(*OH/H₂O) = 1.8–2.7 V).6 SO4** is considered to be more effective than *OH for organic contaminants oxidation due to its electrophilic property7,10 and longer lifetime (SO4** = 30–40 μs, *OH < 1 μs).7,9 It can be generated by peroxynitrousulfate13, persulfate14-16 or sulfate activation,17,18 where sulfate activation is more attractive given that sulfate commonly exists in natural water and wastewater. During SO4** generation via electrochemical activation of sulfate solution, *OH can be produced simultaneously.17 The coupling effects of SO4** and *OH oxidation may facilitate POPs degradation. It is well-known the activity for sulfate activation and POPs degradation mainly depends on properties of electrode. Many electrodes (PbO₂, B doped diamond (BDD), SnO₂ etc.) are found to be active for electrochemical oxidation of pollutants via reactive specialists generated in situ18,20-23 but only BDD can electrochemically activate sulfate to produce SO4**.20-23 Despite the progress has been made, searching for highly active electrodes which can enhance kinetics and decrease energy consumption for electrochemical activation of sulfate solution to generate SO4** and *OH has been actively pursued.

B and N codoped diamond (BND) is an attractive electrode material with high oxygen evolution potential, outstanding electrochemical stability, and chemical inertness.24 Previous works show the synergistic effect of B and N doping into diamond can enhance its electrocatalytic performance.25-26 B and/or N doping can tune the electronic structure of carbon materials and polarize the C atoms adjacent to B and N, resulting in enhanced activity for electrocatalysis.27-29 The polarized carbon atoms, strain and defect sites introduced by B and N doping may act as active sites for electrocatalysis.30,31 Therefore, BND is expected to enhance the performance for electrochemical activation of sulfate solution and POPs degradation. However, BND has not been explored for electrochemical oxidation of pollutants before.

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Herein, BND is explored for electrochemical degradation of POPs via sulfate solution activation. Perfluorooctanoic acid (PFOA) were selected as the targets to evaluate its performance for POPs oxidation. The B and N codoping effect on electrochemical oxidation of PFOA via sulfate solution activation was investigated as well as the reactive specials responsible for PFOA oxidation. The mechanism for PFOA mineralization was proposed based on intermediate analysis.

**MATERIALS AND METHODS**

**Chemicals and Materials.** All chemicals with high purity (analytical and HPLC grade) were used as received without further purification. Perfluorocarboxylic acids (C2−C8, 96−98%) were purchased from J&K Scientific, Ltd. Acetonitrile and methanol were obtained from Sigma-Aldrich. The other reagents including sodium sulfate, sodium nitrate, sodium perchlorate, ammonium acetate and tert-butanol were supplied by Sinopharm Chemical Reagent Co., Ltd. Nanodiamond powder (50 nm) was purchased from Beijing Grish Hitech Co. Ti substrates (>99.9%) were purchased from Central Iron & Steel Research Institute. Milli-Q water was used for all the experiments.

**Preparation of BND, BDD, and NDD Electrodes.** BND, BDD, and NDD films were deposited on Ti substrates by hot filament chemical vapor deposition (HFCVD). The Ti sheet was polished by sandpaper, and ultrasonically washed by ethanol and ultrapure water for 10 min, respectively. To further polish its surface and facilitate diamond nucleation, Ti sheet was ultrasonically pretreated for 20 min in nanodiamond suspension with acetone as solvent. BND film deposition was performed on the pretreated Ti for 12 h with a gas mixture of CH4 (2.5%)/H2 (85%)/N2 (2.5%)/B2H6 (10%) at 600 °C (substrate temperature) and 600 Pa. The total gas flow rate is 100 sccm and temperature ramping rate is about 10 °C/min. For comparison, BDD and NDD electrodes were prepared under the same conditions without N2 and B2H6, respectively. (The cost and scalability for BND preparation are discussed in the Supporting Information, SI.)

**Electrochemical Experiments.** Electrochemical degradation of PFOA was performed in a three-electrode system with homemade H cell and batch mode. Doped diamond was used as working electrode, Pt foil, and Ag/AgCl (saturated KCl) as the counter electrode and reference electrode, respectively. The anodic chamber and cathodic chamber were separated by Nafion 117 membrane. 0.05 M Na2SO4 was used as electrolyte. 30.0 mL Na2SO4 electrolyte was filled on each chamber. The distance between working electrode and counter electrode was 2.5 cm. The effective area of working electrode was 10.5 cm². Chronopotentiometric electrolysis of PFOA were conducted at current density of 0.5−4.0 mA cm⁻² on CHI 660 potentiostat. To investigate the effect of sulfate activation on PFOA degradation, NaNO3 (79.4 mM) or NaClO4 (81.8 mM) with the same conductivity as 0.05 M Na2SO4 (8.4 mS cm⁻¹) were also used as electrolytes for electrochemical oxidation of PFOA. The initial solution pH for the mixture of electrolyte and PFOA was 4.8 without pH adjustment, which was not controlled during PFOA degradation and decreased to 4.2 after PFOA degradation for 2 h at 4.0 mA cm⁻². For selected PFOA degradation experiments, tert-butanol and methanol were added into 0.05 M Na2SO4 electrolyte as radical scavengers with final concentration of 1.0 and 1.5 M.

**Analytical Methods.** PFOA concentration was measured by Waters 2695 HPLC equipped with a C18 column (4.6 mm × 250 mm × 5.0 μm) and UV detector. Isocratic elution was used with acetonitrile and 20 mM sodium dihydrogen phosphate (pH 2.5) as mobile phase at flow rate of 1.0 mL min⁻¹. The intermediates of PFOA degradation were analyzed by liquid chromatography-Triple Quadrupole mass spectrometer (Agilent 1100−6410) with C18 column (2.1 mm × 100 mm × 3.5 μm) and a mixture of acetonitrile (A)/10 mM ammonium acetate (B) as mobile phase. The mobile phase increased linearly from 40% A (initial) to 90% A in 9 min and kept at 90% for 3 min, followed by returning to 40% A in 6.5 min and held at 40% for 2.0 min. Its flow rate was 0.25 mL min⁻¹. A negative ESI multiple reaction monitoring (MRM) mode was adopted for intermediates identification. The capillary potential was 4 kV and gas temperature was 350 °C. Total organic carbon (TOC) was tested by a TOC analyzer (multi N/C 2100, Analytik Jena, Germany).

**RESULTS AND DISCUSSION**

**BND Electrode Characterization.** The morphology of synthesized BND electrode was observed from scanning electron microscope (SEM). As shown in Figure 1a, a continuous and crack free BND film is covered on Ti substrate. The BND film consists of pyramidal particles with edges and corners. The grain size of BND is about 50−200 nm. In the X-ray diffraction (XRD) spectrum (Figure 1b), diffraction peaks at 43.9° and 75.3° appear on BND, which arises from (111) facet and (220) facet of cubic diamond. The sharp peaks indicate BND has good crystallinity. The peaks located at 35.2°, 63.1°, and 70.7° are attributed to TiC. These peaks usually can be observed when carbon films are deposited on Ti substrate. X-ray photoelectron spectroscopy (XPS) analysis shows peaks...
around 186.9 and 400.5 eV arise from B−C and N−C bonds (Figure S1), revealing B and N atoms have been doped into diamond lattice. The B doped into BND is 1.8 at%, while its N content is 0.8 at%.

Electrochemical oxidation of PFOA by BND electrode. The performance of BND electrode for POPs degradation was evaluated by using PFOA as a representative pollutant. Figure 2a shows PFOA is rapidly degraded on BND electrode with 0.05 M Na₂SO₄ as electrolyte. Its removal efficiency enhances gradually as current density increases from 0.5 to 4.0 mA cm⁻² (potentials in Figure S2). A high PFOA removal efficiency of 99.3% is achieved within 1.5 h at current density of 4.0 mA cm⁻². All the PFOA oxidation processes follow pseudo-first-order kinetics (Figure S3). The kinetic constant for PFOA oxidation is 2.40 h⁻¹ at current density of 4.0 mA cm⁻². It increases fast (1.14 h⁻¹ to 1.93 h⁻¹) when current density increases from 2.0 mA cm⁻² to 3.0 mA cm⁻². Although the rate constant further increases to 2.40 h⁻¹ at 4.0 mA cm⁻², the rate increase becomes less pronounced compared with that from 2.0 mA cm⁻² to 3.0 mA cm⁻².

Therefore, current density of 4.0 mA cm⁻² was selected for the subsequent PFOA degradation experiments. Interestingly, BND exhibits significantly enhanced PFOA degradation rate (2.40 h⁻¹ at 4.0 mA cm⁻², corresponding to ~2.5 V vs SCE) compared with other electrodes reported (0.52–2.22 h⁻¹), even though these electrodes operated under much higher current density (20.0 mA cm⁻²) or potential (3.37 vs SCE).

To further investigate the performance of BND electrode for PFOA mineralization, total organic carbon (TOC) removal efficiency were determined during PFOA degradation at 2.0–4.0 mA cm⁻² (0.05 M Na₂SO₄). Figure 2b shows TOC removal improves noticeably at higher current density. After electrochemical oxidation of PFOA for 3 h, TOC removal efficiency is 77.4% at 4.0 mA cm⁻² (PFOA concentration and TOC removal efficiency versus charge are shown in Figure S4).

These results suggest BND electrode is efficient for decomposing PFOA to CO₂ at low current density. The impact of B and N codoping on PFOA oxidation were probed by comparing the performance of BND electrode with B doped diamond (BDD) and N doped diamond (NDD) electrodes. SEM images (Figure S5) show both BDD and NDD films are composed of pyramidal particles, which cover the Ti substrates without noticeable crack. XRD patterns (Figure S6) illustrate BDD and NDD are cubic diamond with (111) facet and (220) facets (diffraction peaks related to Ti and TiC also can be observed on BDD and NDD electrodes, the same as BND electrode). CV curves reveal BND, BDD and NDD electrodes have similar oxygen evolution potential (Figure S7). Thus, BND, BDD and NDD electrodes have similar morphology, oxygen evolution potential and identical crystal structure. XPS analysis reveal the B content of BDD (1.8 at%) and N content of NDD (0.9 at%) are similar to those of BND (1.8 at% B and 0.8 at% N, Table S1). During PFOA oxidation (Figure 3a), BDD presents slightly higher PFOA removal efficiency (92.8% in 2 h) than NDD (86.4% in 2 h). As expected, both of their PFOA removal efficiencies are much lower than that of BND (99.3% in 1.5 h) under the same conditions (0.05 M Na₂SO₄, 4.0 mA cm⁻²). The kinetic constant for PFOA oxidation is 1.2 h⁻¹ on BDD and 1.0 h⁻¹ on NDD (Figure S8a). Note that PFOA oxidation rate on BND is 2.0–2.4 times greater than those on BDD and NDD. TOC removal efficiency on BND is also much higher (Figure S8b). As BND, BDD, and NDD electrodes have identical crystal structure, similar morphology and dopant content, the enhanced performance of BND electrode could be attributed...
to B and N co-doping effect. B and N co-doping improves the electron transfer rate of doped diamond electrode (Figure S9). The electron-deficient B and electron-rich N can induce active sites for electrocatalysis, which play important roles in different elementary reactions during electrocatalytic process, and thereby result in lower potential and improved kinetics for performance in Na$_2$SO$_4$.

Thus, BND shows better performance than BDD and NDD for PFOA oxidation via electrochemically activate sulfate solution. The stability of BND electrode for electrochemical oxidation was examined by 20 consecutive PFOA degradation experiments (batch mode) at the highest current density applied ($4.0$ mA cm$^{-2}$). Its PFOA removal efficiency exhibits no obvious change during 20 consecutive PFOA degradation experiments (Figure 3b), implying BND electrode is stable and reusable for electrochemical oxidation of POPs. The good durability of BND is originated from the chemical and mechanical stability of diamond,$^{39}$ which is important for cost-effective advanced oxidation techniques.

**Effects of Electrolytes and Specific Radical Scavengers on PFOA Oxidation.** The possible oxidative species electrogenerated from sulfate solution activation include SO$_4^{2-}$, *OH, and S$_2$O$_8^{2-}$. To probe which species contributed to the superior performance of BND for electrochemical oxidation, PFOA degradation was also conducted in NaNO$_3$ and NaClO$_4$ electrolytes with the same conductivity as 0.05 M Na$_2$SO$_4$ (8.4 mS cm$^{-1}$) given that both nitrate and perchlorate ions are usually inert during electrochemical oxidation process. Linear sweep voltammograms of BND show its current density at Na$_2$SO$_4$ is larger than those at NaNO$_3$ and NaClO$_4$ (Figure S11b). Since *OH can be produced from all the three electrolytes, the enhanced performance in Na$_2$SO$_4$ may be attributed to active species electrogenerated from sulfate activation. Both SO$_4^{2-}$ and S$_2$O$_8^{2-}$ species can be produced from sulfate activation (Figure S11b).

**Figure 4.** PFOA oxidation on BND electrode (a) at 0.05 M Na$_2$SO$_4$ (8.4 mS cm$^{-1}$), NaNO$_3$ (8.4 mS cm$^{-1}$), NaClO$_4$ (8.4 mS cm$^{-1}$) electrolytes and (b) at 0.05 M Na$_2$SO$_4$ with the presence of methanol or tert-butanol, current density of $4.0$ mA cm$^{-2}$.
Electrochemically oxidized to $SO_4^{2-}$ again on BND. The continuous regeneration of $SO_4^{2-}$ may promote PFOA oxidation by $SO_4^{2-}$. Considering $SO_4^{2-}$ oxidation via electron-transfer and $OH$ oxidation via hydrogen abstraction and addition to unsaturated bonds, $SO_4^{2-}$ oxidation combined with $OH$ oxidation may promote contaminants oxidation kinetics.

**PFOA Oxidation Mechanism.** The organic intermediates produced during electrochemical oxidation of PFOA on BND electrode (0.05 M Na$_2$SO$_4$, 4.0 mA cm$^{-2}$) were determined by LC-MS-MS. The intermediates identified are short-chain perfluorinated carboxylic acids (PFCAs). Figure 5a shows the time dependent concentration of these short-chain PFCAs. Their concentrations first increase gradually with time, and then decrease after reaching the maximum values. At the initial 1 h of PFOA degradation, perfluorooctanoic acid (C$_8$F$_{17}$COOH), perfluoroheptanoic acid (C$_7$F$_{15}$COOH) and perfluoropentanoic acid (C$_5$F$_{11}$COOH) are the main intermediates. The concentration of C$_5$F$_{11}$COOH increases during the first 0.67 h, and then declines over time after achieving maximum at 0.67 h, while concentrations of C$_7$F$_{15}$COOH and C$_8$F$_{17}$COOH starts to decrease after reaching maximum at 1 h. Further electrolysis results in increased concentrations of perfluorobutanoic acid (C$_4$F$_{9}$COOH), perfluoropropionic acid (C$_3$F$_{7}$COOH) and trifluoroacetic acid (C$_3$F$_{7}$COOH). Their concentrations decline after 2 h electrolysis. These results can be explained by that the produced PFCAs intermediate is further oxidized to shorter chain PFCAs, followed by mineralization to CO$_2$, which can be revealed by the high TOC removal efficiency of 93.7% at 4 h (Figure S13). The low concentrations of all PFCAs intermediates after 2 h electrolysis suggest PFOA can be effectively mineralized by BND electrode.

The C mass balance during PFOA oxidation process was investigated to examine whether the main organic intermediates have been identified. Figure 5b shows the C mass balance calculated from $(n_C$ of undegraded PFOA + $n_C$ of PFCAs intermediates)/$n_C$ of initial PFOA. A high C recovery rates of 90.7%–96.2% are obtained during 3 h of PFOA oxidation on BND electrode (4.0 mA cm$^{-2}$, 0.05 M Na$_2$SO$_4$), suggesting the main organic intermediates have been detected. The F mass balance is calculated from $(n_F$ of undegraded PFOA + $n_F$ of PFCAs intermediates + $n_F$ ion)/$n_F$ of initial PFOA, which is 90.3%–93.6% during 3 h of PFOA oxidation (Figure 5c). The defluorination efficiency is 76.8% after 3 h.

The possible mechanism for PFOA degradation (Figure 6) is proposed based on the PFCAs intermediates analysis and the reported pathways for PFOA oxidation by $SO_4^{2-}$ and $OH$ radicals. 14,35,36,38 As radical quenching experiments reveal they are mainly responsible for PFOA oxidation on BND. For $SO_4^{2-}$ oxidation, direct electron transfer occurs between $SO_4^{2-}$ and carboxylic group of PFOA (C$_8$F$_{17}$COOH) due to its electrophilic property, leading to the formation of C$_8$F$_{17}$COO$^+$ and subsequent Kolbe decarboxylation reaction which transfers C$_8$F$_{17}$COO$^+$ to C$_7$F$_{15}$COO$^+$. The produced C$_7$F$_{15}$COO$^+$ reacts with oxygen and proton in solution and transfers to C$_7$F$_{15}$OH (C$_7$F$_{15}$COOH). As C$_7$F$_{15}$COOH is unstable, it will convert to C$_6$F$_{13}$COF by intramolecular rearrangement, which will further undergo hydrolysis and then generate C$_6$F$_{13}$COOH. Meanwhile, PFOA can be oxidized by $OH$, where PFOA loses one electron at anode as it is difficult to be oxidized by $OH$ directly, followed by decarboxylation reaction, and then the formed C$_7$F$_{15}$COO$^+$ reacts with $OH$, resulting in C$_7$F$_{15}$OH formation, which is further converted to C$_6$F$_{13}$COOH by the same pathway mentioned above. For both pathways, the formed C$_6$F$_{13}$COOH intermediate will undergo the same CF2 unzipping reactions as PFOA and transfer to C$_5$F$_{11}$COOH. The CF2 unzipping reactions will continue to occur until PFCAs are oxidized to CO$_2$.

**Environmental Implications.** This study demonstrates that oxidation, direct electron transfer occurs between $SO_4^{2-}$ and carboxylic group of PFOA (C$_8$F$_{17}$COOH) due to its electrophilic property, leading to the formation of C$_8$F$_{17}$COO$^+$ and subsequent Kolbe decarboxylation reaction which transfers C$_8$F$_{17}$COO$^+$ to C$_7$F$_{15}$COO$^+$. The produced C$_7$F$_{15}$COO$^+$ reacts with oxygen and proton in solution and transfers to C$_7$F$_{15}$OH (C$_7$F$_{15}$COOH). As C$_7$F$_{15}$COOH is unstable, it will convert to C$_6$F$_{13}$COF by intramolecular rearrangement, which will further undergo hydrolysis and then generate C$_6$F$_{13}$COOH. Meanwhile, PFOA can be oxidized by $OH$, where PFOA loses one electron at anode as it is difficult to be oxidized by $OH$ directly, followed by decarboxylation reaction, and then the formed C$_7$F$_{15}$COO$^+$ reacts with $OH$, resulting in C$_7$F$_{15}$OH formation, which is further converted to C$_6$F$_{13}$COOH by the same pathway mentioned above. For both pathways, the formed C$_6$F$_{13}$COOH intermediate will undergo the same CF2 unzipping reactions as PFOA and transfer to C$_5$F$_{11}$COOH. The CF2 unzipping reactions will continue to occur until PFCAs are oxidized to CO$_2$.
abundant in natural aqueous environments, \( \text{SO}_4^{2-} \) generation via sulfate activation is more economical and sustainable than persulfate or peroxymonosulfate activation. For aquatic system with chloride, \( \text{SO}_4^{2-} \) mediated oxidation can be hindered.\(^{40,41}\) Most importantly, BND electrode exhibits fast kinetics and low energy consumption for POPs degradation via sulfate solution activation, as revealed by its high PFOA oxidation rate (2.4 \( h^{-1} \)) at low current/potential (4.0 mA cm\(^{-2} \) and ~2.5 V). Its current efficiencies for PFOA oxidation are 1.2–1.6\% (4.0 mA cm\(^{-2} \) at 1.0–1.5 h), much higher than values reported.\(^{35,36}\) The future challenge will be further improving its efficiency. Besides, the BND electrode we proposed for sulfate activation is composed of C, B, and N, which is reusable for a long time and can avoid the potential contamination caused by metals or persulfate/peroxymonosulfate added. This study proposed a new electrocatalytic materials (BND) for simultaneously generating \( \text{SO}_4^{2-} \) and \( \bullet \text{OH} \) via sulfate solution activation. It can significantly enhanced POPs oxidation kinetics, decrease cost (energy consumption, electrolytes cost), and avoid secondary pollution, which is appealing for water treatment.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b06130.

- XPS spectrum of BND, PFOA removal kinetics of BND at sulfate, chronopotentiometric curve, SEM images and XRD spectra of BDD and NDD, B/N contents of three electrodes, and PFOA removal kinetics of BDD and NDD at sulfate and BND at nitrate and perchlorate (PDF)

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Notes

The authors declare no competing financial interest.

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