Self-healing Co₃O₄@Fe₃O₄/cellulose Blend Membranes Efficiently Degrade Perfluorooctanoic Acid in the Visible Light-driven Photo-fenton System

Wenqiang Chen

Shaanxi University of Science and Technology Xi'an Campus: Shaanxi University of Science and Technology

Chen Hou (✉ houchen@sust.edu.cn)

Shaanxi University of Science and Technology Xi'an Campus: Shaanxi University of Science and Technology <https://orcid.org/0000-0003-0981-672X>

Yang Wang

Shaanxi University of Science and Technology Xi'an Campus: Shaanxi University of Science and Technology

Linhui Fu

Shaanxi University of Science and Technology Xi'an Campus: Shaanxi University of Science and Technology

Sufeng Zhang

Shaanxi University of Science and Technology Xi'an Campus: Shaanxi University of Science and Technology

Jianzhi Wang

Wuhan Institute of Technology

Research Article

Keywords: Perfluorooctanoic acid, Cellulose, Heterogeneous catalysis, Photo-Fenton, Vitrimer

Posted Date: September 14th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-862635/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

$\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ was synthesized by in-situ self-assembly strategy coating rod-like MOF-derived Fe_3O_4 with Co_3O_4 nanoparticles and blending with cellulose solution, further applied in the visible light-driven photo-Fenton system for PFOA degradation. In addition, $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}/\text{Vitrimers}$ was obtained to explore the application of self-healing property in photo-Fenton field and the result turned out to be good self-healing capacity for small cracks. In comparison, $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ can degrade around 94.5% PFOA within 180 min in reaction system, which shows better degradation capacity than others catalyst. Moreover, $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ was reused by rinsing with ultra-pure water and the degradation capacity was still 80.4% after five cycles. In this system, the results of Electron paramagnetic resonance analysis (EPR) and scavenger experiment suggested that PFOA degradation was a co-dependent mechanism via photogenerated electrons, photogenerated holes (h^+) and various radical species, rather than a single active constituent. The degradation pathway of PFOA also was proposed based on UHPLC-MS analysis.

1. Introduction

Perfluorooctanoic acid (PFOA), as a typically perfluorinated compound (PFCs), have been used in many products including packing materials, surfactants and nonstick cookware (Park et al., 2020). PFOA is frequently found in drinking water, wildlife and human serum, owing to its high energy carbon-fluorine bonds (C-F , 485 kJ mol^{-1}) and bioaccumulation (Chen et al. 2021; Elanchezhian et al. 2021). More significantly, it has been confirmed that PFOA lead to severely diseases for human health, such as reproductive problems, thyroid disease, and cancer (Blake et al. 2018). Hence, it is increasingly urgent for human health to remove PFOA from environmental medium through efficient and cost-effective methods.

Recently, advanced oxidation processes (AOPs), by active radical species achieving degradation, have shown prominent advantage in organic pollutants degradation field, due to virtue of removal high efficiency and thoroughness. However, the Fenton/Fenton-like is considered to be ineffective for PFOA degradation in some reports, as hydroxyl radicals ($\cdot\text{OH}$) is inactive to PFOA (Trojanowicz et al. 2018). To address this issue, a few researches found $\cdot\text{OH}$ radical can effectively degrade PFOA when extra external energies are introduced to assist Fenton/Fenton-like. Tang et al. reported that the removal rate of PFOA was more than 95% within 5 h in $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ system, while low PFOA removal efficiency achieved in $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system (Tang et al. 2012). The result reveals the feasibility of photo-Fenton in the degradation of PFOA, whereas UV is high energy consumption and must be reacted under strict conditions. Obviously, the visible light is more cost-effective application in photo-Fenton system because of low energy consumption and mild conditions. So selecting the suitable catalyst is pivotal for constructing visible light-driven photo-Fenton system.

Ferroferric oxide (Fe_3O_4), as traditional Fenton catalysts, still draws considerable concern in wastewater treatment on account of its high stability, efficiency and recyclable ability (Jiao et al. 2018). Currently,

Fe_3O_4 have been reported to achieve excellent photocatalytic activity under visible light irradiation (Liang et al. 2020; Xie et al. 2020). The Fe_3O_4 derived from Fe-MOFs show higher specific surface area and porosity than bulk Fe_3O_4 material because the framework structure of MOFs is retained during thermal treatment. For these characters, the MOF-derived Fe_3O_4 is considered as an ideal catalyst material for photo-Fenton system. Moreover, the heterojunction construction is regarded as more efficient strategy than single semiconductors to enhance photocatalytic activity, which can reinforce the utilization ratio of visible light, furnish abundant charge transport channels and shorter migration distance (Feng et al. 2019). Meanwhile, compared with several transition metal ions, cobalt ions (Co^{2+}) not only exhibit superior photocatalytic activity under visible light irradiation, but also is an earth-abundant metallic element (Warang et al. 2013). Accordingly, in-situ coating Co_3O_4 nanoparticles on the surface of porous Fe_3O_4 ($\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$) by self-assembly strategy to form heterojunction for reducing the electron-hole recombination of pure Fe_3O_4 may obviously promote catalytic activity of catalyst.

Cellulose is one of the most abundant biomass materials in nature. Due to its interesting properties, namely, low-cost, sustainability and biocompatibility, cellulose is considered as a great potential raw material for making environmentally friendly products (Hou et al. 2021). When cellulose is dissolved in NaOH/urea/thiourea aqueous media, it can be easily molded into composite membranes by blending catalyst and the hydrophilic of regenerated cellulose can improve the accessibility of reaction solution to the surface of composite materials. In addition, the introduction of cellulose alleviates the agglomeration phenomenon of transition metal oxides catalysts like Fe_3O_4 and Co_3O_4 , and further reinforcing degradation performance and recyclability (Li et al. 2020). Furthermore, in recent years, various self-healing materials have been reported to use as reinforcement and molding agent for improving the cycle stability of products in different fields. Vitrimers, a cross-linked polymer material, can be reprocessed to achieve self-healing via exchange reactions at a certain temperature and maintain the same number of cross-links and covalent bonds (Lossada et al. 2019; Zhao et al. 2019). Therefore, it is good attempt to endow composite membranes with self-healing property by conjunction with vitrimer.

Herein, $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ and $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose/Vitrimer}$ ($\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose/V}$) blend membranes are synthesized by using cellulose as composite material matrix to blend with $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$, and further applied in the photo-Fenton system for PFOA removal and self-healing property exploration, respectively. In this system, $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ not only active H_2O_2 to generate $\cdot\text{OH}$ radicals, but also take advantage of photocatalysis to promote decarboxylation for assistance $\cdot\text{OH}$ degradation of PFOA. Meanwhile, cellulose endows composite material superior hydrophilic and recyclability. The catalytic performance of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ is also evaluated in detail by changing various parameters. Moreover, the reasonable degradation mechanism and pathway are proposed on the basis of the identified intermediates of PFOA degradation. Although the degradation rate of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose/V}$ for PFOA slightly decreases than that of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$, the degradation rate of PFOA can retain at 81.3%. What is more, the self-healing property and decreasing leached metal ions of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose/V}$ are positive for degradation process.

2. Experimental Methods

2.1. Reagents and materials

Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hydrogen peroxide (H_2O_2), N,N-dimethylformamide (DMF), sodium hydroxide (NaOH), ammonium hydroxide, HPLC-grade acetonitrile and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) purchased from Damao Chemical Reagent Factory. Fumaric acid and perfluorooctanoic acid (PFOA) were obtained from Aladdin Co., China. Anhydrous ethanol (EtOH) and *tert*-butanol (TBA) were obtained from Ante Food Co., Ltd. All chemical reagents were directly used without further purification and all solutions were prepared using ultra-pure water, obtained from a Milli-Q system.

2.2. Synthesis of MOF-derived Fe_3O_4 and $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$

The MOF-derived Fe_3O_4 was obtained via the thermolysis under N_2 atmosphere at 600°C for 4 h, and the details were described in supporting information (Scheme 1(a)). For the synthesis of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$, Fe_3O_4 (0.3 g) was added into 13 mL of H_2O and 13 mL of $\text{C}_2\text{H}_5\text{OH}$ solution with string for 1 h to form homogeneous suspension. Then the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) was added into the obtained suspension under mechanical agitation for 3 h. After 1.25 mL ammonium hydroxide was added under stirring for 1 h, the resultant mixture was poured into a 100-mL Teflon-lined stainless steel autoclave and reacted at 170°C for 8 h. The $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ was washed with ultra-pure water and EtOH for three times and vacuum dried at 60°C overnight (Scheme 1(b)).

2.3. Synthesis of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ and $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose/V}$

Initially, 100 g solvent system of alkali/urea/thiourea/water (8/6/8/78 wt%) was pre-cooled to -12.5°C for 1 h (Hou et al. 2021). Subsequently, 2.0 g of cotton pulp cellulose was added to the obtained solution and stirred to give 2 wt% cellulose solution at ambient temperature. While for $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ synthesis, a certain amount of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ (2.5, 5, 10 and 15 wt % based on the total weight of cellulose) was added into cellulose solution with ultrasonic agitation for 4 h. Afterward, 5.0 g of blended solution was poured into a mould and heated to lost its fluidity at 80°C . Then, the mould was placed in ultra-pure water to rinse for 2 h and dried by freeze-drying for 4 h. The $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose/V}$ was prepared by directly dripping vitrimer solution on the $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ (The synthesis route of vitrimer was obtained in the Supplementary data, Fig. S1.). Then, $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ was heated at 60°C for 1 h to evaporate the CH_2Cl_2 and heated at 90°C for 12 h (Scheme 1(c)).

Scheme. 1 Schematic representation of the steps to prepare $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose/V}$ blend membranes.

2.4. Characterization methods

Co₃O₄@Fe₃O₄ nanoparticle and blend membranes were characterized by X-ray diffraction (XRD, D8 Advance), Fourier transform infrared spectra (FTIR, Vector-22), Uv-vis-near-infrared spectrometer (UV-VIS-NIR, Cary 5000), Scanning electron microscopy (SEM, FEI Verios 460), X-ray photoelectron spectrometry (XPS, Thermo ESCALAB 250XI), Electrochemical station (CHI830D/832D), Electron paramagnetic resonance (EPR, EMXmicro-6/1/P/L), High-performance liquid chromatography (HPLC, Waters 1525), Ion chromatograph (IC, 940 Metrohm), Inductively coupled plasma-atomic emission spectrometry (ICP-AES, PE OPTIMA 2100DV), Total organic carbon (TOC, Vario TOC), Ultra-high-performance liquid chromatograph tandem mass spectrometer (UHPLC-MS, QEXACTIVE). The detailed information of those characteristics is shown in the Supplementary Material.

2.5. Degradation experiment and analysis

100 mL of PFOA solution (20 mg/L) was poured into a 250 mL of conical bottle at 25°C. Initially, a blend membrane was immersed in PFOA solution to achieve adsorption equilibrium in dark. Subsequently, a certain dose of H₂O₂ was added into reaction system and the capacity of PFOA degradation contrasted under xenon lamp (300 W) or darkness with magnetic stirring. Thereafter, at 30 min intervals, 0.1 mL of reaction solution was extracted and filtered for measuring the concentration of PFOA by high-performance liquid chromatograph (HPLC). Meanwhile, the intermediates of PFOA were analyzed by ultra-high-performance liquid chromatograph tandem mass spectrometer (UHPLC-MS). The test parameters can be obtained in the Supplementary data.

In order to evaluate the kinetic mechanism, the pseudo-first-order model was employed to interpret the experimental data by the following Eq. (1):

$$\ln\left(\frac{C_0}{C_t}\right) = kt$$

1

where k is pseudo-first-order rate constant (min^{-1}), C_0 (mg/L) is initial PFOA concentration and C_t (mg/L) is PFOA concentration at time t (min).

3. Results And Discussion

3.1. Morphologic and structure characterization

The SEM images were obtained to analyze the morphologies of Fe-MOFs, Fe₃O₄, Co₃O₄@Fe₃O₄, Co₃O₄@Fe₃O₄/cellulose and Co₃O₄@Fe₃O₄/cellulose/V. As shown in Fig. 1(a), the original Fe-MOFs were obtained by solvothermal method exhibited regular rod-like morphology with an average size of 2.4 μm in length and 0.5 μm in diameter. After thermal treatment, Fe₃O₄ still retained the analogous rod-like structure of Fe-MOFs, while the lengths and diameter of Fe₃O₄ were decreased to about 2.2 μm and 0.3

lar Co₃O₄ nanoparticles were observed in Fig.

S2(a-c) with the average diameter of around 30–40 nm and found obvious agglomeration phenomenon. From Fig. 1(c), the rod-like $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ was synthesized when Co_3O_4 nanoparticles were compactly coated on the surface of Fe_3O_4 by *in-situ* self-assembly strategy and the sizes of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ were slightly larger than those of Fe_3O_4 . From the macroscopic view (Fig. 1(d, e)), compared with cellulose, the surface of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ can be notably observed plentiful nanoparticles. Furthermore, the loaded status of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ nanoparticles was shown in the inset of Fig. 1 (e). In addition, a layer of polymer was covered on the surface of cellulose membrane after vitrimers was coated (Fig. 1 (f)).

Figure 1 SEM images of Fe-MOFs (a), Fe_3O_4 (b), $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ (c), cellulose (d), $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ (e), cellulose and $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}/\text{V}$ (f). The inset displayed in Fig. 1 (e) show the high magnification SEM of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$.

FTIR spectra were measured from 400 to 4000 cm^{-1} to exhibit the obtained materials of functional groups (Fig. 2(a)). The characteristic peaks at 3163 cm^{-1} of cellulose, $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ and $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}/\text{V}$ represented the -OH groups on cellulose. For Fe-MOFs, the peak at 1589 and 1388 cm^{-1} was assigned to ν (C-O) bond and asymmetric stretching of carboxylate group, respectively. For $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ and $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$, the low intensity peaks at 586 and 661 cm^{-1} were characteristic of the Fe-O stretching vibration of Fe_3O_4 and the Co-O stretching vibration of Co_3O_4 , respectively. With vitrimer incorporation, the peak at 1751 cm^{-1} attributed to the C = O functional group in the $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}/\text{V}$ (Hou et al. 2020; Zhao et al. 2017; Zhao et al. 2019). These results showed that the $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ catalyst was successfully obtained by hydrothermal method, which were further loaded onto cellulose membranes and incorporated vitrimer.

Figure 2 FTIR spectra of Fe-MOFs, Co_3O_4 , Fe_3O_4 , $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$, $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$, cellulose and $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}/\text{V}$ (a); XRD pattern of that (b); The insets in (b) show a local enlarged view of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$.

XRD patterns of these materials (Fig. 2(b)) were collected to confirm the crystallographic structure. For pure Fe-MOFs, the obvious diffraction peaks were observed but were complex and overlapped. However, the diffraction peaks of MOF-derived Fe_3O_4 and hydrothermal synthesis of Co_3O_4 were utterly identical to those of spinel of Fe_3O_4 (JCPDS NO.43-1003) and Co_3O_4 (JCPDS NO.88-0866), respectively.

Furthermore, the similar peaks those of pure Fe_3O_4 and Co_3O_4 were discovered on XRD pattern of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$. This phenomenon demonstrated that Co_3O_4 was successfully loaded on the Fe_3O_4 by *in-situ* solvothermal method. As shown in Fig. 2(b), the diffraction peaks of regenerated cellulose membranes exhibited positioned at ($2\theta =$) 12.6°, 20.1° and 21.7°, which demonstrated the cellulose I structure was converted to cellulose II structure after alkalization (French 2013). From the insets in Fig. 2(b), a part of diffraction peaks of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ were showed on XRD pattern of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ and positioned at 30.3°, 35.7° and 36.9°. The result proved that $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$

es by blending and regeneration methods.

Furthermore, the XPS spectroscopy of $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4/\text{cellulose}$ was obtained to confirm the surface elemental composition and the structure of blend membranes. According to the XPS survey spectra (Fig. S3), $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4/\text{cellulose}$ blend membranes main consists of C, O, Co and Fe elementals. Nevertheless, owing to uniformly distributed of $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$ in the cellulose membranes, only a little Fe element and Co element can be detected on the surface of $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4/\text{cellulose}$ by XPS. Figure 3(a) displayed the C 1s XPS spectra of $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4/\text{cellulose}$, where it was observed clearly that the peak of C 1s can be grouped into three main peaks (284.9, 286.5 and 287.9 eV), corresponding to C-C/C-H, C-O and C = O, respectively (Hu et al., 2018; Zhuang et al., 2020). As shown in Fig. 3(b), the O 1s XPS spectra can be divided into two peaks at 530.9 and 532.5 eV, ascribing to Fe-O/Co-O and C-O, respectively (Liang et al. 2020; Liu et al. 2018).

Figure 3 XPS spectra of $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4/\text{cellulose}$: (a) C 1s and (b) O 1s.

To investigate the photocatalytic properties of composite materials, the UV-vis DRS of pure Fe_3O_4 , pure Co_3O_4 and $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$ were recorded and compared. As shown in Fig. 4(a), the three samples had excellent adsorption band response in the whole wavelength range from 200 to 800 nm, indicating these materials can efficiently utilize visible light and UV. Compared with $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$, the spectra of Fe_3O_4 had no obvious absorption edge through the visible light wavelength range because of its typical metallic character (Wang et al. 2019). On the basis of Tauc plot, the band gap energy (E_g) of pure Fe_3O_4 , pure Co_3O_4 and $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$ were calculated to be 2.13, 2.10 and 2.12 eV, respectively (Fig. 4(b)) (Wang et al. 2014; Zhao et al. 2017). Furthermore, the flat band potential (E_{FB}) of pure Fe_3O_4 , pure Co_3O_4 and $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$ were evaluated by Mott-Schottky curve. As shown in Fig. 4(c), these materials were typical p-type semiconductors due to the negative slope of their curves. The E_{FB} of pure Fe_3O_4 , pure Co_3O_4 and $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$ were around 1.45, 1.04 and 1.31 eV versus SCE (equivalent to 1.69, 1.28 and 1.55 eV vs. NHE), respectively. As is well known, the valence band (E_{VB}) position was more positive by 0.1 eV than the E_{FB} for p-type semiconductor (Hou et al. 2021). Therefore, the E_{VB} of these materials were around 1.79, 1.38 and 1.65 eV vs. NHE. Using the equation $E_{\text{CB}} = E_{\text{VB}} - E_g$, the conduction band (E_{CB}) of the three samples were calculated to be approximately -0.34, -0.72 and -0.47 eV vs. NHE, respectively.

Figure 4 The optical properties of pure Fe_3O_4 , pure Co_3O_4 and $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$: (a) UV-vis DRS spectra; (b) the corresponding Tauc plot; (c) The Mott-Schottky curves; (d) Transient photocurrent response (in a 0.5 M Na_2SO_4 solution).

As shown in Fig. 4(d), the charge carrier migration of pure Fe_3O_4 , pure Co_3O_4 and $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$ was detected and compared by electrochemical measurements under visible light irradiation. From the photocurrent verses time (I-t) curves of pure Fe_3O_4 , pure Co_3O_4 and $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$, these electrode photocurrent response curves can be changed by controlling xenon lamp, indicating the separation or recombination of photo-generated electron-hole pairs (Yu et al. 2016).

3.2 Photo-Fenton performances on PFOA degradation

Figure 5(a) showed the degradation performances of as-prepared catalysts for PFOA. In dark, although $\cdot\text{OH}$ radical can be produced by $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ activated H_2O_2 , the degradation rate of PFOA was only 16.1% and the rate constant was 0.0009 min^{-1} (Fig. S4(a)). Nevertheless, under visible light irradiation, 44.8% of PFOA was degraded by photocatalysis of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ within 180 min. In addition, the degradation rate of PFOA can be increased to 94.5% when $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ and H_2O_2 were present in reaction solution under visible light irradiation. These phenomena implied that it was ineffective to degrade PFOA by Fenton/Fenton-like alone and $\cdot\text{OH}$ may play a key role to facilitate the PFOA hydroxylation in Photo-Fenton system (Javed et al. 2020). Furthermore, the removal rate and rate constant of PFOA decreased to around 81.3% and 0.0089 min^{-1} , respectively, when $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}/\text{V}$ was used to degrade PFOA under the same condition. The phenomenon can be attributed to vitrimer which may inhibit the catalyst ability to degrade PFOA. Meanwhile, as shown in Table S1, PFOA was efficiently degradation under UV irradiation but that of inefficiently under visible light irradiation in previous studies. In comparison, this work improved the degradation capacity of PFOA under visible light irradiation.

As shown in Fig. 5(b), different H_2O_2 dosages were added to explore the catalytic performance. When the H_2O_2 concentration increased from 10 mM to 30 mM, the degradation rate increased with the H_2O_2 concentration in reaction solution and the rate constants also increased from 0.0046 min^{-1} to 0.0151 min^{-1} (Fig. S4(b)). However, the degradation rate decreased when the H_2O_2 concentration was increased to 40 mM. A part of $\cdot\text{OH}$ was captured by excess H_2O_2 to generate the weak oxidation capacity $\text{HO}_2\cdot$, which not only reduced the catalytic capacity of reaction system but also accelerated the consumption of H_2O_2 (Pereza et al. 2002). Hence, the optimal concentration of H_2O_2 was 30 mM in the Photo-Fenton system.

Figure 5(c) exhibited the impact of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ dosages on the degradation rate of PFOA. The degradation performance was promoted obviously when the weight percent of catalyst was increased from 2.5% ($k = 0.0038 \text{ min}^{-1}$, Fig. S4(c)) to 10% ($k = 0.0151 \text{ min}^{-1}$, Fig. S4(c)), it is because the number of active sites increased with the weight percent of catalyst. Yet degradation rate changed slightly when the weight percent of catalyst was increased 15%. Excessive catalysts were difficult to uniformly disperse on the cellulose membrane, resulting in the agglomeration of catalysts, reducing the active sites and increasing the scattering of the irradiated light (Wang et al. 2017). To save resources and ensuring degradation effect, the weight percent of catalyst was set as 10% in this work.

The pH value not only affected the surface charge of the catalyst but also ionization state of PFOA and consequently to impacted the degradation performance. In the Fig. 5(d), various initial solution pH was evaluated during photo-Fenton process. Under visible light irradiation for 180 min, the best degradation rate of PFOA was 94.5% at pH 3 while was gradually decreased to 79.6% and 65.9% as pH increased to 5 and 7, respectively. The degradation rate of PFOA further obviously decreased to 32.5% ($k = 0.0017 \text{ min}^{-1}$, Fig. S4(d)) when the pH was increased to 10. In basic solution, $\cdot\text{OH}$ was unstable and abundant $\cdot\text{OH}$ was

consumed by reacting with OH⁻ ions, leading to slow down degradation of PFOA (Xu et al. 2020). Moreover, Fig. 5(e) exhibited the zeta potential of Co₃O₄@Fe₃O₄/cellulose in different pH value. It can be clearly observed that the zeta potential decreased with the increased solution pH, and the zero point of charge (pHzpc) of Co₃O₄@Fe₃O₄/cellulose was 5.2. In previous study, the acid dissociation constant (pKa) of PFOA had been reported to be approximately 2.8 (Shang et al. 2018). In consequence, both PFOA as well as the surface of Co₃O₄@Fe₃O₄/cellulose were negatively charged when the reaction solution pH was higher than 5.2. It was difficult for Co₃O₄@Fe₃O₄/cellulose to adsorb PFOA due to repulsion each other, restraining the photo-Fenton efficacy. Hence, the degradation capacity of Co₃O₄@Fe₃O₄/cellulose for PFOA decreased at higher pH as a result of describing above reasons.

Figure 5(f) presented the degradation capacity of the Co₃O₄@Fe₃O₄/cellulose after five cycles. Although the PFOA degradation capacity slightly decreased after the first degradation cycle on account of the loss of nanoparticles rinsed, the degradation rate of PFOA was still 80.4% after five cycles. Meanwhile, the leached Fe and Co (C_{Fe} and C_{Co}) were only 0.05 and 0.49 ppm after first degradation cycle, respectively. What is more, the C_{Fe} and C_{Co} remained at 0.05 and 0.42 ppm when Co₃O₄@Fe₃O₄/cellulose/V was used as catalyst (Fig. S5), which suggested that Co₃O₄@Fe₃O₄/cellulose and Co₃O₄@Fe₃O₄/cellulose/V membranes had more outstanding stability than Co₃O₄@Fe₃O₄ powder. The phenomenon may be caused by the interception of cellulose and the protective effect of vitrimer..

Figure 5 (a) Degradation efficiency of PFOA in different reaction systems within 180 min; (b) Effect of H₂O₂ concentration; (c) Effect of catalysts dose; (d) Effect of solution pH; (e) the pH effect on the zeta potential of Co₃O₄@Fe₃O₄/cellulose. (f) Reusability of blend membrane. Reaction conditions: PFOA = 20 mg/L, H₂O₂ = 30 mM (10, 20, 30 and 40 mM in Fig. 5(b)), pH = 3.0 (2.5, 3.0, 5.0, 7.0 and 10.0 in Fig. 5(d)).

Figure 6(a) presented the time-dependent changes of F⁻ concentration within 180 min in H₂O₂/Co₃O₄@Fe₃O₄/cellulose/visible light system (H₂O₂/membrane/visible light system). It was clear that the concentration of F⁻ was a positive relation with time, which implied that the C-F bonds were cleaved through photo-Fenton. The concentration of F⁻ was around 6.5 mg/L within 180 min by ion chromatograph (IC) which equivalent to defluorination ratio of 47%. However, the concentration of F⁻ was around 13.1 mg/L by theoretical calculation under optimal degradation condition. This result was explained from two main aspects. On one hand, Co₃O₄@Fe₃O₄/cellulose can adsorb F⁻ due to porous structure of cellulose membranes (Wang et al. 2019). On the other hand, some kinds of short-chain perfluorocarboxylates (PFCAs) were generated during the degradation process (Gomez-Ruiz et al. 2018). And these short-chain PFCAs were detected and analyzed by UHPLC-MS to confirm this claim in this work. The total organic carbon (TOC) removal was also measured to evaluate the mineralization rate of PFOA under optimum degradation condition and shown in Fig. 6(b). The TOC removal efficiency increased continuously over time, and reached 67% after degradation of PFOA for 180 min. These results indicated that the prepared Co₃O₄@Fe₃O₄/cellulose can efficiently mineralize PFOA through visible light-driven photo-Fenton system.

Figure 6 (a) Concentration of F^- by $Co_3O_4@Fe_3O_4$ /cellulose degradation of PFOA; (b) TOC removal efficiency by $Co_3O_4@Fe_3O_4$ /cellulose degradation of PFOA. Reaction conditions: PFOA = 20 mg/L, H_2O_2 = 30 mM, and pH = 3.0.

3.3 Photo-Fenton mechanisms

3.3.1 Active constituents

In the H_2O_2 /membrane/visible light system, to confirm the involvement of various active radical species, several kind of scavengers (TBA, BQ and $Na_2C_2O_4$) were added to system for scavenging $\cdot OH$, superoxide radical ($O_2^{\cdot -}$) and photogenerated holes (h^+), respectively. From the Fig. 7(a), almost of PFOA was degraded under optimal experimental conditions within 180 min. However, when 20 mmolL⁻¹ of TBA or BQ was added in the reaction solution, the degradation rate of PFOA reduced to 57.1% and 73.2%, with the rate constants of 0.0045 min⁻¹ and 0.0068 min⁻¹ (Fig. 7(b)), respectively. The results confirmed that $\cdot OH$ and $O_2^{\cdot -}$ radicals took part in reaction process and promoted the degradation of PFOA. Similarly, when 20 mmolL⁻¹ of $Na_2C_2O_4$ was added in the H_2O_2 /membrane/visible light system, the degradation performance was significantly depressed, with the degradation rate of 26.3% and the rate constant of 0.0017 min⁻¹, indicating that h^+ played major roles for PFOA degradation in the this system. In a word, the scavenger experiment result suggested that PFOA degradation was a co-dependent mechanism via h^+ and various radical species, rather than a single radical or h^+ alone in the H_2O_2 /membrane/visible light system. Meanwhile, to sustain the results of the scavenger experiment, the active radical species further were probed by EPR spectra with DMPO. As shown in Fig. 7(c), whether under visible light irradiation or dark condition, the signals of DMPO- $\cdot OH$ (peak intensity ratio = 1:2:2:1) were observed. However, the signals intensity of DMPO- $\cdot OH$ were stronger under visible light irradiation, due to visible light acceleration of Fe^{2+}/Fe^{3+} cycle during H_2O_2 activation process (Wu et al. 2020). From Fig. 7(d), the signals of DMPO- $O_2^{\cdot -}$ (peak intensity ratio = 1:1:1:1) only were observed under visible light irradiation because $O_2^{\cdot -}$ was produced by photocatalysis of $Co_3O_4@Fe_3O_4$ /cellulose.

Figure 7 (a) The effect of scavengers (TBA, BQ and $Na_2C_2O_4$) on PFOA degradation [PFOA = 20 mg/L, H_2O_2 = 30 mM, pH = 3.0, Scavenger = 20 mM]; (b) the constant rate of scavenger experiment; (c) EPR spectra obtained of $\cdot OH$; (d) EPR spectra obtained of $O_2^{\cdot -}$.

3.3.2 Generation mechanism of active constituents

As shown in Fig. 8(a), Co 2p XPS spectra of pure Co_3O_4 and $Co_3O_4@Fe_3O_4$ were obtained for exploring the electronic structure. Compared with pure Co_3O_4 , the Co 2p states of $Co_3O_4@Fe_3O_4$ exhibited a negative shift. Analogously, the Fe 2p states of $Co_3O_4@Fe_3O_4$ showed significantly positive shift relative to those of pure Fe_3O_4 (Fig. 8(b)). In normal condition, the positive shift of XPS spectra suggested a weakened effect of electron density, and the negative shift hinted an enhance effect of electron density

Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js phenomenon indicated the presence of electrons

migration from Fe_3O_4 to Co_3O_4 at the interface of $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$ and formed a electric field at the interface of $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$. In this case, the photogenerated electrons was driven to transfer from the Co_3O_4 to the Fe_3O_4 and h^+ was driven to transfer from the Fe_3O_4 to the Co_3O_4 under visible light irradiation. This transference of photogenerated electrons was proposed to be the typical type II heterojunction migration system..

The degradation processes of PFOA were shown in Fig. 8(c), a part of photogenerated electrons on the CB of Co_3O_4 were migrated to Fe_3O_4 under visible light irradiation and further reacted with dissolved O_2 of solution to reduce into $\text{O}_2^{\cdot-}$ ($\text{O}_2/\text{O}_2^{\cdot-}$, - 0.33 eV vs. NHE), as shown in Eqs. (2–3) (Wang et al. 2020). Nevertheless, $\text{O}_2^{\cdot-}$ was not the main active species due to the low concentration of dissolved O_2 in solution. Meanwhile, the trapped photogenerated electrons by the Fe^{3+} accelerated the redox cycle of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and facilitate the generation of $\cdot\text{OH}$ radical, Eqs. (2, 4–5) (Wu et al. 2020). For $\cdot\text{OH}$ radical, it was only generated by Fenton process because the reduction potential $\text{OH}^-/\cdot\text{OH}$ (2.40 eV vs NHE) was more positive than that of Co_3O_4 (1.38 eV vs NHE) (Zhang et al. 2019). However, the h^+ in the VB- Co_3O_4 was a key factor for the PFOA decarboxylation process due to its strong oxidation property.

Figure 8 (a) Co 2p XPS spectra of pure Co_3O_4 and $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$; (b) Fe 2p XPS spectra of pure Fe_3O_4 and $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$; (c) Type-II heterojunction reaction mechanism.

2

3

4

5

3.3.3 Degradation pathway of PFOA

To explore the degradation pathway of PFOA during the photo-Fenton reaction, the reaction solution at different times were detected by UHPLC-MS and the degradation intermediates of PFOA were listed in Table S2 and Fig. S6. A total of four shorter-chain perfluorocarboxylates (PFCAs) were identified in these solution samples, while only perfluoroheptanoic acid (PFHpA) was detected within 30 min. The phenomenon indicated that longer PFCAs intermediates were formed in the first step of degradation and photo-Fenton proceeds. According to above

experimental results and literature work (He et al. 2020; Hou et al. 2021; J. Wang et al. 2020; Wang et al. 2021), the possible degradation pathway was proposed in Fig. 9. Initially, the decarboxylation process of PFOA was accomplished to generate perfluorinated alkyl radicals ($\cdot C_7F_{15}$) by $O_2^{\cdot-}$ and h^+ at the beginning stage of reaction, as shown in Eqs. (6–7). Subsequently, $\cdot C_7F_{15}$ further reacted with $\cdot OH$ radical and formed $C_7F_{15}OH$ (Eq. (8)). However, the $C_7F_{15}OH$ is very sensitive in solution and easily eliminated H^+ and F^- to generate $C_6F_{13}COF$ (Eq. (9)). Finally, $C_6F_{13}COF$ was further hydrolyzed into $C_6F_{13}COOH$ (PFHpA) (Eq. (10)). The PFHpA and residual PFOA were degraded to form shorter chain intermediates by similar decomposition procedure.

6

7

8

9

10

Figure 9 Proposed degradation pathway of PFOA in the H_2O_2 /membrane/visible light system.

3.4 Self-healing performances and mechanism

In addition, the collision of stirring was inevitable in the catalytic process. Therefore, some small cracks were caused on the surface of the blend membranes under magnetic stirring, which was negative for the recyclability of catalyst. As shown in Fig. 10(a), a small crack was clearly observed on the surface of $Co_3O_4@Fe_3O_4$ /cellulose/V blend membrane after some degradation cycles. However, the small crack can be healed when $Co_3O_4@Fe_3O_4$ /cellulose/V was heated at $90^\circ C$ overnight (Fig. 10(b)). The self-healing properties was mainly attributed to the trans-carbonation exchange reactions between amidogen groups and carbonate at the cracks interface, which can quickly and efficiently form of covalent bonds across the cracks (Zhao et al. 2019).

Figure 10 Self-healing ability of cracks on $Co_3O_4@Fe_3O_4$ /cellulose/V surface.

4. Conclusion

In summary, the $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ and $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}/\text{V}$ blend membranes were synthesized, which was further employed to degrade PFOA in visible light-driven photo-Fenton system. Compared with the degradation performance of pure Fe_3O_4 or pure Co_3O_4 , when $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ was added into reaction solution, the degradation rate of PFOA was increased to 94.5% within 180 min under visible light irradiation. Moreover, $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ can retain 80.4% degradation rate after five cycles. These experiments showed $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ had outstanding stability. For $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}/\text{V}$ blend membrane, although the rate constant of PFOA slightly decreased to 81.3% within 180 min because of incorporating vitrimer, the materials showed good self-healing property when some small cracks were caused on the surface. According to the scavenger experiment results, these scavengers were able to restrain the degradation performance by scavenging different active constituents. The phenomenon indicated that photogenerated electrons, h^+ , $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ radicals were involved in the PFOA degradation process, and achieved degradation via a co-dependent mechanism, rather than a single active constituent. Meanwhile, the signals of $\text{DMPO}\cdot\text{OH}$ and $\text{DMPO}\text{-}\text{O}_2^{\cdot-}$ were observed in EPR spectra under different conditions. The degradation pathway of PFOA also was proposed based on UHPLC-MS analysis, which indicated longer chain intermediates were formed in the initial stage and further oxidized into shorter chain intermediates with the photo-Fenton proceeds. This strategy provides new insight to develop the visible light-driven photo-Fenton system and the application of vitrimer in the degradation of organic pollution.

Declarations

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21806096), the China Postdoctoral Science Foundation (2020M683412), the Natural Science Basic Research Plan in Shaanxi Province (2019JQ-529), the Special Research Program of Shaanxi Provincial Department of Education (20JK0541).

Availability of data and material My research didn't generate any data or I reused existing data.

Compliance with Ethical Standards

Conflict of interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Research involving human participants and/or animals

We have no research involving human participants and/or animals.

Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js

References

- Blake BE, Pinney SM, Hines EP, Fenton SE, Ferguson KK (2018) Associations between longitudinal serum perfluoroalkyl substance (PFAS) levels and measures of thyroid hormone, kidney function, and body mass index in the Fernald Community Cohort. *Environ Pollut* 242: 894-904. <https://doi.org/10.1016/j.envpol.2018.07.042>
- Chen C, Ma Q, Liu F, Gao J, Li X, Sun S, Zhang W (2021) Photocatalytically Reductive Defluorination of Perfluorooctanoic Acid (PFOA) using Pt/La₂Ti₂O₇ Nanoplates: Experimental and DFT Assessment. *J Hazard Mater* 419, 126452. <https://doi.org/10.1016/j.jhazmat.2021.126452>
- Elanchezhian S S, Preethi J, Rathinam K, Njaramba L K, Park C M (2021) Synthesis of magnetic chitosan biopolymeric spheres and their adsorption performances for PFOA and PFOS from aqueous environment. *Carbohydr Polym* 267: 118165. <https://doi.org/10.1016/j.carbpol.2021.118165>
- Fan J, Zhang S, Xu Y, Wei N, Wan B, Qian L, Liu Y (2020) A polyethylenimine/salicylaldehyde modified cellulose Schiff base for selective and sensitive Fe(3+) detection. *Carbohydr Polym* 228 115379. <https://doi.org/10.1016/j.carbpol.2019.115379>
- Feng XB, Ju HM, Song TH, Fang TS, Liu WC, Huang W (2019) Highly Efficient Photocatalytic Degradation Performance of CsPb(Br_{1-x}Cl_x)₃-Au Nanoheterostructures. *ACS Sustan, Chem. Eng* 7: 5152-5156. <https://doi.org/10.1021/acssuschemeng.8b06023>
- French AD (2013) Idealized powder diffraction patterns for cellulose polymorphs. *Cellulose* 21: 885-896. <https://doi.org/10.1007/s10570-013-0030-4>
- Gomez-Ruiz B, Ribao P, Diban N, Rivero M J, Ortiz I, Urtiaga A (2018) Photocatalytic degradation and mineralization of perfluorooctanoic acid (PFOA) using a composite TiO₂-rGO catalyst. *J Hazard Mater* 344: 950-957. <https://doi.org/10.1016/j.jhazmat.2017.11.048>
- He X, Sun B, He M, Chi H, Wang Z, Zhang W, Ma J (2020) Highly efficient simultaneous catalytic degradation and defluorination of perfluorooctanoic acid by the H₂O₂-carbon/MnO₂ system generating O₂ and •OH synchronously. *Appl Catal B-Environ* 227: 119219. <https://doi.org/10.1016/j.apcatb.2020.119219>
- Hou C, Chen WQ, Fu LH, Zhang SF, Liang C, Wang Y (2021) Efficient degradation of perfluorooctanoic acid by electrospun lignin-based bimetallic MOFs nanofibers composite membranes with peroxydisulfate under solar light irradiation. *Int J Biol Macromol* 174: 319-329. <https://doi.org/10.1016/j.ijbiomac.2021.01.184>
- Hou C, Chen WQ, Fu LH, Zhang SF, Liang C, Wang Y (2020) Facile synthesis of a Co/Fe bi-MOFs/CNF membrane nanocomposite and its application in the degradation of tetrabromobisphenol A. *Carbohydr* [20.116731](https://doi.org/10.1016/j.carbpol.2020.116731)

- Hou C, Fu LH, Wang Y, Chen WQ, Zhang SF, Wang JZ (2021) Core-shell magnetic Fe₃O₄/CNC@MOF composites with peroxidase-like activity for colorimetric detection of phenol. *Cellulose* 42: 1-16. <https://doi.org/10.1007/s10570-021-04117-w>
- Hou C, Fu LH, Wang Y, Chen WQ, Chen F, Zhang SF, Wang JZ (2021) Co-MOF-74 based Co₃O₄/cellulose derivative membrane as dual-functional catalyst for colorimetric detection and degradation of phenol. *Carbohyd Polym* 273: 118548. <https://doi.org/10.1016/j.carbpol.2021.118548>
- Hu B, Liu Y, Wang Z, Song Y, Wang M, Zhang Z, Liu, C (2018) Bimetallic-organic framework derived porous Co₃O₄/Fe₃O₄/C-loaded g-C₃N₄ nanocomposites as non-enzymic electrocatalysis oxidation toward ascorbic acid, dopamine acid, and uric acid. *Appl Surf Sci* 441: 694-707. <https://doi.org/10.1016/j.apsusc.2018.02.093>.
- Javed H, Lyu C, Sun R, Zhang D, J.J Alvarez P (2020) Discerning the inefficacy of hydroxyl radicals during perfluorooctanoic acid degradation. *Chemosphere* 247: 125883. <https://doi.org/10.1016/j.chemosphere.2020.125883>.
- Jiao Y, Wan C, Bao W, Gao H, Liang D, Li J (2018) Facile hydrothermal synthesis of Fe₃O₄@cellulose aerogel nanocomposite and its application in Fenton-like degradation of Rhodamine B. *Carbohyd Polym* 189: 371-378. <https://doi.org/10.1016/j.carbpol.2018.02.028>.
- Li H, Zhang L, Lu H, Ma J, Zhou X, Wang Z, Yi C (2020) Macro-/nanoporous Al-doped ZnO/cellulose composites based on tunable cellulose fiber sizes for enhancing photocatalytic properties. *Carbohyd Polym* 250: 116873. <https://doi.org/10.1016/j.carbpol.2020.116873>
- Liang Q, Gao W, Liu C, Xu S, Li Z (2020) A novel 2D/1D core-shell heterostructures coupling MOF-derived iron oxides with ZnIn₂S₄ for enhanced photocatalytic activity. *J Hazard Mater* 392: 122500. <https://doi.org/10.1016/j.jhazmat.2020.122500>
- Liu C, Fu Y, Xia Y, Zhu C, Hu L, Zhang K, Kang Z (2018) Cascaded photo-potential in carbon dot-hematite system driving overall water splitting under visible light. *Nanoscale* 10: 2454-2460. <https://doi.org/10.1039/C7NR08000J>
- Lossada F, Guo JQ, Jiao DJ, Groeer S, Bourgeat-Lami E, Montarnal D, Walther A (2019) Vitrimers Chemistry Meets Cellulose Nanofibrils: Bioinspired Nanopapers with High Water Resistance and Strong Adhesion. *Biomacromolecules* 20: 1045-1055. <https://doi.org/10.1021/acs.biomac.8b01659>
- Low J, Jiang C, Cheng B, Wageh S, Al-Ghamdi AA, Yu J (2017) A Review of Direct Z-Scheme Photocatalysts. *Small Methods* 1: 1700080. <https://doi.org/10.1002/smtd.201700080>
- Park M, Wu S, Lopez IJ, Chang JY, Karanfil T, Snyder SA (2020) Adsorption of perfluoroalkyl substances (PFAS) in groundwater by granular activated carbons: Roles of hydrophobicity of PFAS and carbon

Pereza M, Torrades F, Domenech X, Peral J (2002) Fenton and photo-Fenton oxidation of textile effluents. *Water Res* 36: 2703-2710. [https://doi.org/10.1016/s0043-1354\(01\)00506-1](https://doi.org/10.1016/s0043-1354(01)00506-1)

Shang E, Li Y, Niu J, Li S, Zhang G, Wang X (2018) Photocatalytic degradation of perfluorooctanoic acid over Pb-BiFeO₃/rGO catalyst: Kinetics and mechanism. *Chemosphere* 211: 34-43. <https://doi.org/10.1016/j.chemosphere.2018.07.130>

Tang H, Xiang Q, Lei M, Yan JC, Zhu LH, Zou J (2012) Efficient degradation of perfluorooctanoic acid by UV-Fenton process. *Chem Eng J* 184: 156–162. <https://doi.org/10.1016/j.cej.2012.01.020>

Trojanowicz M, Bojanowska-Czajka A, Bartosiewicz I, Kulisa K. (2018) Advanced Oxidation/Reduction Processes treatment for aqueous perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) – A review of recent advances. *Chem Eng J* 336: 170-199. <https://doi.org/10.1016/j.cej.2017.10.153>

Wang C, Li J, Lv X, Zhang Y, Guo G (2014) Photocatalytic organic pollutants degradation in metal-organic frameworks. *Energy Environ Sci* 7: 2831-2867. <https://doi.org/10.1039/c4ee01299b>

Wang J, Cao C, Wang Y, Wang Y, Sun B, Zhu L (2020) In situ preparation of p-n BiOI@Bi₅O₇I heterojunction for enhanced PFOA photocatalytic degradation under simulated solar light irradiation. *Chem Eng J* 319: 123530. <https://doi.org/10.1016/j.cej.2019.123530>

Wang JZ, Cao CS, Zhang Y, Zhang YQ, Zhu LY (2021) Underneath mechanisms into the super effective degradation of PFOA by BiOF nanosheets with tunable oxygen vacancies on exposed (101) facets. *Appl Catal B-Environ* 286: 119911. <https://doi.org/10.1016/j.apcatb.2021.119911>

Wang Q, Liu M, Zhao H, Chen Y, Xiao F, Chu W, Zhao G (2019) Efficiently degradation of perfluorooctanoic acid in synergic electrochemical process combining cathodic electro-Fenton and anodic oxidation. *Chem Eng J* 378: 122071. <https://doi.org/10.1016/j.cej.2019.122071>

Wang S, Yang Q, Chen F, Sun J, Luo K., Yao F, Zeng G (2017) Photocatalytic degradation of perfluorooctanoic acid and perfluorooctane sulfonate in water: A critical review. *Chem Eng J* 328: 927-942. <https://doi.org/10.1016/j.cej.2017.07.076>

Wang Y, Zhang F, Lin H, Qu F (2019) Biodegradable Hollow MoSe₂/Fe₃O₄ Nanospheres as PDT Enhanced Agent for Multimode CT/MR/IR Imaging and Synergistic Anti-Tumor Therapy. *ACS Appl Mater Inter* 11: 43964-43975. <https://doi.org/10.1021/acsami.9b17237>

Wang Y, Zhu C, Zuo G, Guo Y, Xiao W, Dai Y, Xian Q (2020) 0D/2D Co₃O₄/TiO₂ Z-Scheme heterojunction for boosted photocatalytic degradation and mechanism investigation. *Appl Catal B-Environ* 278: 119298. <https://doi.org/10.1016/j.apcatb.2020.119298>

Warang T, Patel N, Fernandes R, Bazzanella N, Miotello A (2013) Co₃O₄ nanoparticles assembled coatings synthesized by different techniques for photo-degradation of methylene blue dye. *Appl Catal B-*

Environ 132: 204-211. <https://doi.org/10.1016/j.apcatb.2012.11.040>

Wu Q, Yang H, Kang L, Gao Z, Ren F (2020) Fe-based metal-organic frameworks as Fenton-like catalysts for highly efficient degradation of tetracycline hydrochloride over a wide pH range: acceleration of Fe(II)/Fe(III) cycle under visible light irradiation. Appl Catal B-Environ 263:188282. <https://doi.org/10.1016/j.apcatb.2019.118282>

Xie AT, Cui JY, Yang J, Chen YY, Lang JH, Li CX, Dai JD (2020) Graphene oxide/Fe(III)-based metal-organic framework membrane for enhanced water purification based on synergistic separation and photo-Fenton processes. Appl Catal B-Environ 264: 118548. <https://doi.org/10.1016/j.apcatb.2019.118548>

Xu B, Zhou JL, Altaee A, Ahmed MB, Johir MAH, Ren J, Li X (2020) Improved photocatalysis of perfluorooctanoic acid in water and wastewater by Ga₂O₃/UV system assisted by peroxymonosulfate. Chemosphere 239: 124722. <https://doi.org/10.1016/j.chemosphere.2019.124722>

Yu C, Zhou W, Zhu L, Li G, Yang K, Jin R (2016) Integrating plasmonic Au nanorods with dendritic like α -Bi₂O₃/Bi₂O₂CO₃ heterostructures for superior visible-light-driven photocatalysis. Appl Catal B-Environ 184: 1-11. <https://doi.org/10.1016/j.apcatb.2015.11.026>

Zhang Y, Zhou J, Chen X, Wang L, Cai, W (2019) Coupling of heterogeneous advanced oxidation processes and photocatalysis in efficient degradation of tetracycline hydrochloride by Fe-based MOFs: Synergistic effect and degradation pathway. Chem Eng J 369, 745-757. <https://doi.org/10.1016/j.cej.2019.03.108>

Zhao H, Chen Y, Peng Q, Wang Q, Zhao G (2017) Catalytic activity of MOF(2Fe/Co)/carbon aerogel for improving H₂O₂ and •OH generation in solar photo–electro–Fenton process. Appl Catal B-Environ 203: 127-137. <https://doi.org/10.1016/j.apcatb.2016.09.074>

Zhao W, Feng Z, Liang Z, Lv Y, Xiang F, Xiong C, Ni Y (2019) Vitrimers-Cellulose Paper Composites: A New Class of Strong, Smart, Green, and Sustainable Materials. ACS Appl Mater Inter 11: 36090–36099. <https://doi.org/10.1021/acsami.9b11991>

Zhuang Y, Wang X, Zhang L, Kou Z, Shi B (2020) Confinement Fenton-like degradation of perfluorooctanoic acid by a three dimensional metal-free catalyst derived from waste. Appl Catal B-Environ 275: 119101. <https://doi.org/10.1016/j.apcatb.2020.119101>

Figures

Figure 1

SEM images of Fe-MOFs (a), Fe_3O_4 (b), $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$ (c), cellulose (d), $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$ (e), cellulose and $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}/\text{V}$ (f). The inset displayed in Fig. 1 (e) show the high magnification SEM of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$.

Figure 2

FTIR spectra of Fe-MOFs, Co_3O_4 , Fe_3O_4 , $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$, $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$, cellulose and $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}/\text{V}$ (a); XRD pattern of that (b); The insets in (b) show a local enlarged view of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$.

Figure 3

XPS spectra of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$: (a) C 1s and (b) O 1s.

Figure 4

The optical properties of pure Fe_3O_4 , pure Co_3O_4 and $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4$: (a) UV-vis DRS spectra; (b) the corresponding Tauc plot; (c) The Mott-Schottky curves; (d) Transient photocurrent response (in a 0.5 M Na_2SO_4 solution).

Figure 5

5 (a) Degradation efficiency of PFOA in different reaction systems within 180 min; (b) Effect of H_2O_2 concentration; (c) Effect of catalysts dose; (d) Effect of solution pH; (e) the pH effect on the zeta potential of $\text{Co}_3\text{O}_4@\text{Fe}_3\text{O}_4/\text{cellulose}$. (f) Reusability of blend membrane. Reaction conditions: PFOA = 20 mg/L, H_2O_2 = 30 mM (10, 20, 30 and 40 mM in Fig. 5(b)), pH = 3.0 (2.5, 3.0, 5.0, 7.0 and 10.0 in Fig. 5(d)).

Figure 6

(a) Concentration of F⁻ by Co₃O₄@Fe₃O₄/cellulose degradation of PFOA; (b) TOC removal efficiency by Co₃O₄@Fe₃O₄/cellulose degradation of PFOA. Reaction conditions: PFOA = 20 mg/L, H₂O₂ = 30 mM, and pH = 3.0.

Figure 7

(a) The effect of scavengers (TBA, BQ and Na₂C₂O₄) on PFOA degradation [PFOA = 20 mg/L, H₂O₂ = 30 mM, pH = 3.0, Scavenger = 20 mM]; (b) the constant rate of scavenger experiment; (c) EPR spectra obtained of •OH; (d) EPR spectra obtained of O₂•⁻.

Figure 8

Self-healing ability of cracks on $\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4/\text{cellulose}/\text{V}$ surface.

Figure 9

(a) Co 2p XPS spectra of pure Co_3O_4 and $Co_3O_4@Fe_3O_4$; (b) Fe 2p XPS spectra of pure Fe_3O_4 and $Co_3O_4@Fe_3O_4$; (c) Type-II heterojunction reaction mechanism.

Proposed degradation pathway of PFOA in the H₂O₂/membrane/visible light system.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupportingInformation.docx](#)
- [floatimage1.png](#)