CONTENTS

Aquatic environment
Comparison of conventional and inverted A2/O processes: Phosphorus release and uptake behaviors
Rong Qi, Tao Yu, Zheng Li, Dong Li, Takashi Mino, Tadashi Shoji, Kochi Fujie, Min Yang .......................................................... 571
Distribution of heavy metals in sediments of the Pearl River Estuary, Southern China: Implications for sources and historical changes
Feng Ye, Xiaoping Huang, Dawen Zhang, Lei Tian, Yanyi Zeng ................................................................................................................. 579
Removal of arsenate and arsenite from aqueous solution by waste cast iron
Nag-Choi Choi, Song-Bae Kim, Soo-Oh Kim, Jae-Won Lee, Jun-Beum Park .......................................................................................... 589
Effect of artificial aeration on the performance of vertical-flow constructed wetland treating heavily polluted river water
Huiyu Dong, Zhimin Qiang, Tinggang Li, Hui Jin, Weidong Chen ............................................................................................................. 596
A 60-year sedimentary record of natural and anthropogenic impacts on Lake Chenghai, China
Fengyu Gan, Shouliang Huo, Beidou Xi, Jingtian Zhang, Haiqing Liao, Yue Wang, Kevin M. Yeager .................................................. 602
Preparation and application of amino functionalized mesoporous nanofiber membrane via electrospinning for adsorption of Cr(III) from aqueous solution
Ahmed A. Taha, Junlian Qiao, Fengting Li, Bingtu Zhang ...................................................................................................................... 610
Removal of phosphate ions from aqueous solution using Tunisian clays minerals and synthetic zeolite
Noureddine Hamdi, Ezzeddine Srarsa .................................................................................................................................................. 617

Atmospheric environment
Impacts of continuously regenerating trap and particle oxidation catalyst on the NO2 and particulate matter emissions emitted from diesel engine
Zhuha Liu, Yunshan Ge, Jianwei Tan, Chao He, Asad Naeem Shah, Yan Ding, Linxiao Yu, Wei Zhao ................................................................ 624
Dry deposition velocity of total suspended particles and meteorological influence in four locations in Guangzhou, China
Leifu Chen, Shaolin Peng, Jingang Liu, Qianqian Hou .......................................................................................................................... 632
Synthesis, characterization and experimental investigation of Cu-BTC as CO2 absorbent from flue gas
Jiangkun Xie, Naiaqiang Yan, Zan Qu, Shijian Yang .............................................................................................................................. 640
Aerosol effects on ozone concentrations in Beijing: A model sensitivity study
Jun Xu, Yuanhang Zhang, Shaoqing Zheng, Youjiang He ......................................................................................................................... 645
Measurement of air exchange rates in different indoor environments using continuous CO2 sensors
Yan You, Can Niu, Jian Zhou, Yating Liu, Zhipeng Bai, Jiufeng Zhang, Pei He, Nan Zhang ................................................................. 657
Influence of different weather events on concentrations of particulate matter with different sizes in Lanzhou, China
Xinyuan Feng, Shigong Wang .............................................................................................................................................................. 665

Terrestrial environment
Sorption of chlorophenols onto fruit cuticles and potato periderm
Yunxi Li, Yingqing Deng, Baoluang Chen ........................................................................................................................................... 675
Effects of urea and (NH4)2SO4 on nitrification and acidification of Ultisols from Southern China
Deli Tong, Rongkui Xu ........................................................................................................................................................................... 682
Health risk assessment of heavy metals in soils and vegetables from wastewater irrigated area, Beijing-Tianjin city cluster, China
Yanchun Wang, Xiadong Zhang, Zhangwei Wang, Yi Zhang, Bingwen Li, Rolf Vogt ............................................................................ 704

Environmental biology
Ammonium-dependent regulation of aerobic methane-consuming bacteria in landfill cover soil by leachate irrigation
Fan Li, Pengju He, Min Guo, Na Yang, Liming Shao ............................................................................................................................. 711
Steady performance of a zero valent iron packed anaerobic reactor for azo dye wastewater treatment under variable influent quality
Yaozheng Zhang, Yuanwen Liu, Jianwen Jing, Zhiqiang Zhao, Xie Quan ................................................................................................. 720
Identification of naphthalene metabolism by white rot fungus Armillaria sp. F022
Tony Hadibarata, Abdull Rahim Mohd Yusoff, Azmi Aris, Risky Ayu Kristanti .......................................................................................... 728

Environmental health and toxicology
Inhibition of ROS elevation and damage to mitochondrial function prevents lead-induced neurotoxic effects on structures and functions
of AFD neurons in Caenorhabditis elegans
Quili Wu, Peidong Liu, Yinxia Li, Min Du, Xiaojuan Xing, Dayong Wang ...................................................................................... 733

Environmental catalysis and materials
Photodegradation of Norfloxacin in aqueous solution containing algae
Junwei Zhang, Daifang Fu, Jilong Wu ...................................................................................................................................................... 743
Synthesis of TiO2 nanoparticles in different thermal conditions and modeling its photocatalytic activity with artificial neural network
Fatemeh Ghanbary, Nasser Modirshahla, Morteza Khosravi, Mohammad Ali Behnajady ..................................................................... 750
Preparation of Fe3C/latex/SO4 solid solution and its application in Pd-only three-way catalysts
Jianqiang Wang, Meiqing Shen, Jun Wang, Mingshui Cai, Jidong Gao, Jie Ma, Shuangxi Liu ............................................................. 757
Dechlorination of chlorophenols by zero valent iron impregnated silica
Praveena Jiyala Dorathi, Palanivelu Kandasamy ................................................................................................................................. 765
Photocatalytic degradation of perfluorooctanoic acid with β-Ga2O3 in anoxic aqueous solution
Baoxiong Zhao, Mou Lv, Li Zhou ....................................................................................................................................................... 774

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Photocatalytic degradation of perfluorooctanoic acid with $\beta$-Ga$_2$O$_3$ in anoxic aqueous solution

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Abstract
Perfluorooctanoic acid (PFOA) is a new-found hazardous persistent organic pollutant, and it is resistant to decomposition by hydroxyl radical (HO·) due to its stable chemical structure and the high electronegativity of fluorine. Photocatalytic reduction of PFOA with $\beta$-Ga$_2$O$_3$ in anoxic aqueous solution was investigated for the first time, and the results showed that the photoinduced electron ($e^-_{cb}$) coming from the $\beta$-Ga$_2$O$_3$ conduction band was the major degradation substance for PFOA, and shorter-chain perfluorinated carboxylic acids (PFCAs, $C_nF_{2n+1}COOH$, $1 \leq n \leq 6$) were the dominant products. Furthermore, the concentration of $F^-$ was measured by the IC technique and defluorination efficiency was calculated. After 3 hr, the photocatalytic degradation efficiency was 98.8% and defluorination efficiency was 31.6% in the presence of thiosulfate and bubbling $N_2$. The degradation reaction followed first-order kinetics ($k = 0.0239$ min$^{-1}$, $t_{1/2} = 0.48$ hr). PFCAs ($C_nF_{2n+1}COOH$, $1 \leq n \leq 7$) were detected and measured by LC-MS and LC-MS/MS methods. It was deduced that the probable photocatalytic degradation mechanism involves $e^-_{cb}$ attacking the carbonyl of $C_nF_{2n+1}COOH$, resulting in decarboxylation and the generation of $C_nF_{2n+1}$. The produced $C_nF_{2n+1}$ reacted with $H_2O$, forming $C_nF_{2n+1}OH$, then $C_nF_{2n+1}OH$ underwent HF loss and hydrolysis to form $C_nF_{2n+1}COOH$.

Key words: perfluorooctanoic acid; $\beta$-Ga$_2$O$_3$; photocatalytic degradation; defluorination; photoinduced electron

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Introduction
Perfluorocarboxylic acids (PFCAs, $C_nF_{2n+1}COOH$) have recently caused much concern due to their persistence and bioaccumulative properties (Bischel et al., 2010; Niisoe et al., 2010; Houde et al., 2006; Pistocchi and Loos, 2009). Perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$), as a member of the PFCAs’ family, was classified as a likely potential carcinogen by The US EPA’s Science Advisory Board in 2006. Recently, PFOA and its precursors have been globally detected in water (Hansen et al., 2002; So et al., 2004), wildlife (Martin et al., 2004; Kannan et al., 2006) and human beings (Tao et al., 2008; Niisoe et al., 2010). So far, no natural decomposition pathway for PFOA has been reported. Hori (2004) and Moriwaki (2005) indicated that it was difficult for most conventional advanced oxidation processes (AOPs) involving hydroxyl radical (HO·) to decompose PFOA. In recent years many efforts have been made to develop effective decomposition or defluorination processes to destroy PFOA, because shorterchain compounds are less bioaccumulative (Kudo et al., 2010; Scott et al., 2006) and cause milder environmental pollution.

At present, treatments for PFOA mainly include photochemical oxidation and sonochemical methods. Hori (2005, 2008) reported that PFOA could be destroyed by photochemical oxidation in the presence of heteropolyacid (H$_3$PW$_{12}$O$_{40}$) or persulfate (S$_2$O$_8^{2-}$), and F and shorter-chain PFCAs were detected as the major products in aqueous solution. Moriwaki (2005) found that PFOA was pyrolyzed at the interfacial region between the cavitation bubbles and the bulk solution in a sonochemical degradation reaction, and F and shorter-chain PFCAs were also identified in the liquid phase. Vecitis (2008) and Cheng (2008, 2010) studied the sonolysis degradation of PFOA and found that the degradation conformed to first-order kinetics and that PFOA was converted to CO, CO$_2$, F$^-$ and shorter-chain PFCAs. Furthermore, Dillert (2007) reported that PFOA could be decomposed by TiO$_2$ photocatalytic oxidation, but they found that degradation only occurred in strongly acidic aqueous solution (0.1 mol/L HClO$_4$). Panchangam (2009) also proved that PFOA was only efficiently destroyed by TiO$_2$ photocatalytic reaction in strongly acidic solution (0.075–0.1 mmol/L HClO$_4$).

To the best of our knowledge, there has been no report on PFOA degradation in anoxic aqueous solution with a...
semiconductor photocatalytic reaction. Besides the photocatalytic oxidation degradation for POPs, semiconductor photocatalysis also has the ability to reduce organic compounds. Actually photocatalytic reduction is an alternative pathway for the degradation of poly- or per-halogenated organic compounds which are difficult to oxidize further. For example, the simplest perchloroalkane, i.e., CCl₄ was photo-reductively degraded by TiO₂ in the presence of organic electron donors (Chio and Hoffmann, 1995), and ZnS and CdS were also used as photocatalysts for the reductive dehalogenation of halogenated benzene derivatives (Yin et al., 2001).

Ga₂O₃ is a wide bandgap semiconductor and it is mainly used in the photoelectronic field (Zheng et al., 2007); nevertheless it is rarely used as a photocatalyst in wastewater treatment. Compared with TiO₂ (E₇ = 3.2 eV, Eₘ = 4.21 eV), Ga₂O₃ possesses a wider bandgap (E₇ = 4.8 eV) and higher conduction band position (Eₘ = −2.95 eV). Thus, theoretically, the reduction potential of Ga₂O₃ is higher than that of TiO₂, which implies that it is possible for Ga₂O₃ to decompose PFOA. Based on this, we first investigated the photocatalytic decomposition of PFOA with β-Ga₂O₃ in anoxic solution and then deduced the decomposition mechanism.

1 Materials and methods

1.1 Materials

PFCAs (purity > 98%), including PFOA (C₁₂F₂₃COOH), perfluorohexanoic acid (C₁₆F₃₇COOH), perfluorooctanoic acid (C₁₈F₃₇COOH), perfluoropentanoic acid (C₁₀F₂₁COOH), perfluorobutyric acid (C₈F₁₇COOH), perfluoroheptanoic acid (C₇F₁₇COOH) and trifluoroformyl acid (TFA, CF₃COOH), were all purchased from Aldrich Co. (USA). α-Ga₂O₃ powder (purity ≥ 99.9%) was purchased from Aladdin Reagent Co. (China). Methanol, thiosulfate and oxalate were all analytical reagents and purchased from Aladdin Reagent Co. (China). Methanol, thiosulfate and oxalate were all analytical reagents and purchased from Aladdin Reagent Co. (China). High purity water (18.2 MΩ/cm) was used in all experiments was prepared using the Thermo Scientific Barnstead Nanopure Diamond UV™ water purification system (Thermo Scientific, USA).

1.2 Preparation of β-Ga₂O₃ and characterizations

Using α-Ga₂O₃ as raw material, β-Ga₂O₃ was successfully prepared through calcination at 800°C for 4 hr in air. The crystalline phase of β-Ga₂O₃ was analyzed by an X-ray diffraction (XRD) instrument monitored by a D/max-RB system (Cu Kα irradiation, λ = 1.5406 Å, voltage = 40 kV, current = 30 mA, scanning rate = 0.01°/sec, scanning range = 10°–80°). Based on the Brunauer-Emmett-Teller (BET) equation, Ga₂O₃ specific surface areas were obtained using the nitrogen sorption-desorption equipment (NOVA4000, Germany) at 77.3 K. The bandgap energy was derived from the UV-Vis diffuse reflection spectrum measured with a UV-Vis NIR spectrometer (Varian Cary 500, USA).

1.3 Photocatalytic degradation procedure

Photocatalytic degradation of PFOA was performed in a cylindrical quartz reactor with a glass jacket for cooling water circulation. PFOA aqueous solution (100 mL, 75 μmol/L) containing 0.5 g/L β-Ga₂O₃ powder was transferred to the reactor. The UV-C light (λ = 254 nm) was irradiated using a 15 W low-pressure mercury lamp which was placed in the center of the reactor, equipped with a protective quartz tube. High-purity nitrogen gas (P > 99.99%) was supplied to the solution with a flow rate of 40 mL/min. The mixed solution containing PFOA and β-Ga₂O₃ was first bubbled for 3 hr to ensure that the adsorption of PFOA on β-Ga₂O₃ surface and reactor interior had reached equilibrium (in this experiment, the adsorption for PFOA was about 6.4% after 3 hr accompanied with bubbling N₂), then the reaction was started. The initial pH of the PFOA solution (75 μmol/L) was about 4.8 and was not adjusted in the following experiments.

1.4 Ion chromatography

The concentrations of F⁻, S₂O₃²⁻ and SO₄²⁻ were measured with an Ion Chromatography System (ICS-2000, Dionex, Sunnyvale, USA) equipped with an automatic elution generator and separation column (Dionex Ionpac AS11). The column temperature was maintained at 30°C and the injection volume was kept at 25 μL. The eluting phase containing 30 mmol/L KOH was automatically produced by the electrolysis apparatus connected with the chromatography system and the flow rate was set at 1.2 mL/min. Before analysis, all samples were filtered with a 0.45 μm PFTE membrane to remove β-Ga₂O₃ particles.

1.5 LC-MS and LC-MS/MS analysis

The concentrations of PFOA and shorter-chain PFCAs were measured by a Waters Acquity Ulta Performance Liquid Chromatography (LC) system linked with a micromass Quattro Premier Tandem Quadrupole mass spectrometer (Waters, USA). The electrospray negative ion (ES⁻) mode was adopted. The mobile phase consisted of 2 mmol/L ammonium acetate (named as solvent A) and 2 mmol/L ammonium acetate/methanol (named as solvent B), and the flow rate was 0.4 mL/min. A gradient flow mode was used and the flow sequences were as follows: 0–0.5 min, isocratic flow of 30% solvent B and 70% solvent A; 0.5–5.0 min, linear increase of solvent B from 30% to 90%; 5.0–5.1 min: linear increase of solvent B from 90% to 100%; 5.1–6.0 min: hold solvent B at 100%; 6.0–7.0 min: linear decrease of solvent B from 100% to 30%; 7.0–10.0 min: hold solvent B at 30%. Samples were managed by an auto-sampler (Waters, USA) and separated by an Acquity BEH C₁₈ column (2.1 mm × 50 mm, 1.7 μm). Data acquisition of chromatograms or mass spectra was controlled by the MassLynx V 4.1 software. The MS full scan spectrum ranged from m/z 100 to 420 and the scan time was 10.0 min. The concentrations of PFOA and shorter-chain PFCAs were measured with a 7-channel MRM mode. Here, all samples were diluted below 1.0 mg/L and filtered by a 0.22 μm PFTE ultra-filtration.
membrane before analysis.

2 Results and discussion

2.1 Characterizations of β-Ga$_2$O$_3$

The Ga$_2$O$_3$ crystal phase can be characterized by XRD patterns. Figure 1 displays the crystallization of commercial α-Ga$_2$O$_3$ and as-prepared β-Ga$_2$O$_3$. Several characteristic diffraction peaks which belong to the β phase (JCPDS No: 43-1012) clearly appear in the XRD pattern, which shows that β-Ga$_2$O$_3$ can be obtained by the dry calcination method using α-Ga$_2$O$_3$ as raw material. According to the BET equation, the specific surface area of as-prepared β-Ga$_2$O$_3$ decreases slightly to 27.8 m$^2$/g, compared with that of α-Ga$_2$O$_3$ (32.1 m$^2$/g), which suggests that a few particles co-aggregate during the transformation of the crystal phase.

The bandgap energy ($E_g$) of as-prepared β-Ga$_2$O$_3$ can be obtained from the UV-Vis diffuse reflection spectrum (Fig. 2). The value of $E_g$ (4.7 eV) can be obtained from the intersection point (258 nm) of the tangent and the X-axis, which is in agreement with the reported value of 4.8 eV for pure powder (Xu and Schoonen, 2005).

![Fig. 1 X-ray diffraction patterns of α-Ga$_2$O$_3$ and β-Ga$_2$O$_3$ prepared by calcination at 800°C for 4 hr in air.](image1)

![Fig. 2 UV-Vis diffuse reflection spectrum of as-prepared β-Ga$_2$O$_3$.](image2)

2.2 Photocatalytic decomposition

Three experiments including direct photodegradation and β-Ga$_2$O$_3$ photocatalytic degradation in the presence of N$_2$ or O$_2$ were carried out. From Fig. 3, it appears that PFOA is hardly destroyed by direct photodegradation, only 4.8% PFOA is degraded after 3 hr, and 43.6% PFOA is destroyed in the presence of N$_2$, but only 10.7% PFOA is decomposed when O$_2$ instead of N$_2$ is supplied. This is to say that the photoinduced hole or HO· is not the protagonist decomposing PFOA. Thus the sole actor involved in PFOA degradation is photoinduced electrons ($e^-_{cb}$). In fact, $e^-_{cb}$ has a powerful ability to reduce halogen-containing compounds through dehalogenation reactions (Chio and Hoffmann, 1995). The conclusion that PFOA is destroyed by $e^-_{cb}$ can be explained by the bandgap structures of β-Ga$_2$O$_3$ and TiO$_2$. β-Ga$_2$O$_3$ has a more negative reduction potential (–1.55 V (NHE)) than TiO$_2$ (–0.29 V (NHE)). This reveals that $e^-_{cb}$ coming from the β-Ga$_2$O$_3$ possesses a more powerful reduction ability, compared with that coming from TiO$_2$.

2.3 Photocatalytic defluorination

To research the fate of fluorine atoms, the F$^-$ concentration was measured. Here, defluorination ($R$, %) and transformation degree of fluorine (denoted as $D_F$) are introduced and defined by Eqs. (1) and (2).

$$R(\%) = \frac{C_F^- \times 100}{15 \times C_{PFOA}}$$  \hspace{1cm} (1)

$$D_F = \frac{C_F^-}{15 \times (C_{PFOA} - C_{PFOA})}$$  \hspace{1cm} (2)

where, $C_F^-$ is the molar concentration of fluoride ions; $C_{PFOA}$ and $C_{PFOA}$ are the initial and t time molar concentrations of PFOA, respectively. The relationship of defluorination and $D_F$ with reaction time is shown in Fig. 4. It is observed that defluorination increases with reaction time and arrives at 15.7% after 3 hr, while $D_F$ changes only a little from 0.273 at 30 min to 0.286 at 3 hr, which suggests that the relationship between the generation of F$^-$ and degradation of PFOA is fixed. This is to say that about four fluorine atoms are transformed to F$^-$ and released.

![Fig. 3 (a) Direct photodegradation and β-Ga$_2$O$_3$ photocatalytic decomposition in the presence of N$_2$ or O$_2$, respectively.](image3)
to the solution when one molecule PFOA is completely degraded, and the remaining fluorine atoms may exist in other intermediates.

2.4 Effect of pH on photocatalytic decomposition

pH is one of the important factors in the photocatalytic reaction, because it influences the charge state of the photocatalyst and ionization degree of the pollutant. The photocatalytic decomposition of PFOA was conducted at four different pH values, i.e., 4, 7, 9, and 11, and results are presented in Fig. 5. The results show that the decomposition efficiency decreases with increasing pH. Although the most-cited pKₐ value of PFOA is 2.8 in the literature (Goss, 2008), recently an argument has been put forth that the pKₐ value of PFOA may be as low as –0.5 based on analogy considerations and molecular modeling. According to this estimated pKₐ value, PFOA molecules completely ionize in the investigated pH range (pH 4–11) and exist in the form of C₄F₁₅COO⁻ anions. The above analysis can be approved by the following Reaction (3) and Eqs. (4) and (5).

\[
C_7F_{15}COOH \rightarrow C_7F_{15}COO^- + H^+ \quad (3)
\]

\[
K_a = \frac{C_{H^+} \times C_{C_7F_{15}COO^-}}{C_{C_7F_{15}COOH}} = 10^{-pK_a} \times \frac{C_{C_7F_{15}COO^-}}{C_0 - C_{C_7F_{15}COO^-}} \quad (4)
\]

\[
C_{C_7F_{15}COO^-} = \frac{K_a \times C_0}{10^{pH} + K_a} \approx C_0 \quad (5)
\]

where, C₀ is the initial concentration of PFOA. According to Eq. (3), it is observed that the change of pH (4–11) does not affect the ionization of PFOA. However, pH change definitely influences the surface charge state of β-Ga₂O₃. The reported isoelectric point (IEP) of β-Ga₂O₃ is about pH 9 (Kosmulski, 2001), so the surface charge of β-Ga₂O₃ becomes positive when the pH is lower than 9, which is beneficial for the adsorption for C₇F₁₅COO⁻ anions on the β-Ga₂O₃ surface, and negative when the pH is higher than 9, which repels the adsorption of C₇F₁₅COO⁻ anions on the β-Ga₂O₃ surface. As is well known, photocatalytic reaction mainly occurs on the surface of the catalyst, so it is reasonable that the photocatalytic decomposition for PFOA performs better in lower pH solutions where C₇F₁₅COO⁻ is more easily adsorbed on the surface of β-Ga₂O₃.

2.5 Effect of reductive additives on photocatalytic degradation

Based on the above analysis, it is observed that PFOA is decomposed well under a reductive atmosphere. Although N₂ bubbling can drive dissolved O₂ out of an aqueous solution to an utmost degree, residual dissolved O₂ still reacts with e⁻ from to produce H₂O₂, weakening the concentration of e⁻.

To further drive dissolved O₂ and H₂O₂ out of the reaction system, methanol (CH₃OH), S₂O₃²⁻ and oxalate (C₂O₄²⁻) reductive reagents were studied and results are shown in Table 1. Before the investigation on the effects of reductive additives on PFOA degradation, corresponding blank experiments were carried out and results showed that the influences of reductive additives were slight (removal efficiency < 4.6%). It is clearly observed that the addition of reductive reagents accelerates the degradation and defluorination of PFOA, and S₂O₃²⁻ performs best. To some extent, degradation increases with increasing amount of S₂O₃²⁻, and the reason can be explained by the following Reactions ((6)–(7)).

\[
2S_2O_3^{-} + 3O_2 \rightarrow 2SO_4^{2-} + 2SO_2 \quad (6)
\]

\[
S_2O_3^{2-} + 4H_2O_2 \rightarrow 2SO_4^{2-} + 3H_2O + 2H^+ \quad (7)
\]

Furthermore, a phenomenon is observed that the concentration of S₂O₃²⁻ decreases with the reaction time and almost all S₂O₃²⁻ is transformed to SO₄²⁻ at last, suggesting that S₂O₃²⁻ is indeed oxidized by O₂ or H₂O₂.

2.6 Major intermediates and degradation mechanism

As mentioned above, F⁻ is one of the major intermediates in aqueous solution. To further analyze other major products in the liquid phase, a LC-MS full scan was carried out and the spectrum is presented in Fig. 6. Compared with the inset MS full scan spectrum of the PFOA standard...
sample, one series of obvious peaks appears at m/z 413, 363, 313, 263, 213, 163, 113 and the m/z differences between the neighboring peaks are 50. They are assigned to [C_{n}F_{2n+1}COO]^- (1 \leq n \leq 7) and the m/z difference is caused by the loss of the –CF_2 group, which reveals that shorter-chain PFCAs are major intermediates in the reduction reaction. Another series of peaks are present at m/z 369, 319, and 269 and the m/z differences between the neighboring peaks are also 50. These peaks are assigned to [C_{2n}F_{2n+1}COO]^- (5 \leq n \leq 7) groups which originate from C_{n}F_{2n+1}H. Because C_{n}F_{2n+1}H (2 \leq n \leq 4) molecules are gaseous under normal conditions and easily escape from the solution, the peaks at m/z 219, 169 and 119 are not observed in the MS spectrum. Besides these characteristic peaks, there appear intense peaks at m/z 119, 141, 155, 217, but they also emerge in the spectrum of the PFOA standard sample. These peaks are probably caused by solvents or impurities from the PFOA sample.

In the photochemical and sonochemical degradation reactions, the decomposition mechanism involves three steps: decarboxylation of PFOA, elimination of HF from C_{7}F_{15}OH and hydrolysis of C_{6}F_{13}COF. Based on the MS spectrum and chromatograms, the β-Ga_{2}O_{3} photocatalytic decomposition mechanism can be deduced. First, PFOA is ionized to C_{7}F_{15}COO^- and H^+ in water. Then the C_{7}F_{15}COO^- absorbs on the surface of β-Ga_{2}O_{3} and reacts with e_{cb} forming C_{7}F_{15}^*:

\[
C_{7}F_{15}COO^- + e_{cb} \rightarrow C_{7}F_{15}COO^2^- + H^+ \rightarrow \text{C}_{7}F_{15}^* + \text{CO}
\]  

There is a similar study showing that PFOA can be reductively degraded into C_{7}F_{15} and CO by a hydrated electron (e_{cb}) (Park et al., 2009). The C_{7}F_{15}^* produced is very active and quickly reacts with H_{2}O to form C_{7}F_{15}OH. C_{7}F_{15}OH is unstable and easily loses HF, generating C_{6}F_{13}COF which easily hydrolyzes to form C_{6}H_{13}COOH. Then, step by step, C_{5}H_{13}COOH, C_{4}H_{8}COOH, C_{3}H_{6}COOH, C_{2}H_{5}COOH and CH_{3}COOH are produced. In fact, Yamamoto et al. (2007) also observed shorter-chain PFCAs during photodegradation of PFOS in the presence of alkaline 2-propanol and bubbling N_{2}. Perhaps due to a low photodegradation decomposition efficiency (k = 0.93 day^{-1}), only C_{7}F_{15}COOH, C_{6}F_{13}COOH, C_{5}F_{11}COOH were measured. That is to say that shorter-chain PFCAs
are major organic products during PFOA degradation with the reduction method.

3 Conclusions

PFOA was efficiently decomposed by $\beta$-Ga$_2$O$_3$ photocatalytic reduction and photoinduced electrons were the effective species destroying PFOA in anoxic aqueous solution. Photocatalytic degradation and defluorination of PFOA was 98.8% and 31.6% in the presence of $S_2$O$_5^-$ and $N_2$, respectively. Photocatalytic decomposition followed first-order kinetics ($k = 0.0239$ min$^{-1}$, $t_{1/2} = 0.48$ hr), and $F^-$ and shorter-chain PFCAs were the major products during PFOA degradation. Reductive decarboxylation of PFOA was the crucial pathway in the $\beta$-Ga$_2$O$_3$ photocatalytic reaction.

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