



Photocatalytic decomposition of perfluorooctanoic acid by iron and niobium co-doped titanium dioxide

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ABSTRACT

The photocatalytic decomposition of perfluorooctanoic acid (PFOA) in aqueous solution using Fe and Nb co-doped TiO₂ (Fe:Nb-TiO₂) prepared by sol–gel method was investigated. The photocatalytic activity of Fe:Nb-TiO₂ towards PFOA degradation was compared to that of pure TiO₂ synthesized using the same method, and that of the commercially available TiO₂ photocatalyst, Aeroxide TiO₂ P25 (AO-TiO₂ P25). The photocatalysts were characterized by XRD, DRS, BET-N₂ adsorption isotherm, and SEM-EDX techniques and the data were correlated to the photocatalytic activity. Fe:Nb-TiO₂ showed the highest activity compared to the undoped TiO₂ and the commercially available TiO₂. Such activity was attributable to the effects of co-doping both on the physico-chemical properties and surface interfacial charge transfer mechanisms. Perfluorocarboxylic acids (PFCAs) with shorter carbon chain length and fluoride ions were identified as photocatalytic reaction intermediates and products.

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1. Introduction

Perfluorooctanoic acid (PFOA) is a synthetic chemical compound that belongs to a class of fully fluorinated hydrocarbons known as perfluorocarboxylic acids (PFCAs). These compounds are extensively used in the manufacture of fluoropolymers, and in a wide range of industrial applications as surfactants, fire retardants, and oil, stain and grease repellants, because of their hydrophobic and lipophobic properties, and their high chemical and thermal stabilities. PFOA products contain homologues ranging from 4 to 13 carbons, but the concern is particularly focused on products containing 8 carbons, such as PFOA, which account for the majority of the PFOA production and emission to the environment [1]. Due to its negligible vapor pressure, solubility in water, and moderate sorption to solids, PFOA accumulates and persists in surface waters, and resists natural degradation processes [2]. Toxicological studies demonstrated that exposure to PFOA can lead to developmental and reproductive toxicities, liver damage, and possibly cancer [3,4]. With the impending risks posed to the environment, technologies for the decomposition of PFOA in aqueous media should be developed.

Photocatalytic processes had been proven effective in converting organic pollutants in water matrix into mineral acids, CO₂, and

H₂O. Recently, a few studies have been reported on the photocatalytic decomposition of fluorinated compounds. Among these are homogeneous photocatalysis of PFOA using phosphotungstic acid [5], and photochemical oxidation using persulfate [6]. While a considerable amount of PFOA was degraded, these methods require extreme reaction conditions such as very low pH or high pressure. TiO₂-mediated heterogeneous photocatalysis of PFOA and other perfluorinated compounds under relatively mild conditions have been reported using pure TiO₂ and various light sources [7,8], also the investigation on the degradation of a perfluorinated surfactant by gliding arc discharge, with reactive radicals generated by TiO₂ light activation as major agents of decomposition [9]. TiO₂ doped with platinum had been applied to the defluorination of pentafluorobenzoic acid [10], with the enhanced photo-activity attributed to the electron trapping mechanism of Pt.

In this study, the photocatalytic activity of Fe and Nb co-doped TiO₂ towards PFOA decomposition in aqueous solution was investigated and compared to undoped TiO₂ prepared in the same method, and to the commercially available Aeroxide TiO₂ P25.

2. Experimental

2.1. Materials

Perfluorooctanoic acid (PFOA, C₇F₁₅COOH) as well as chemicals for the sol–gel synthesis of Fe and Nb co-doped TiO₂, such as titanium tetraisopropoxide (C₁₂H₂₈O₄Ti), nitric acid, ammonia solution, ferric nitrate [Fe(NO₃)₃·9H₂O], and isopropyl alcohol was purchased from Wako Chemical Co., Japan. Ammonium niobium

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oxalate ($C_4NH_4NbO_9 \cdot nH_2O$) was obtained from Aldrich Chemical Co., USA. Aeroxide TiO₂ P25 was supplied by Nippon Aerosil Co., Japan. LC grade methanol and ammonium acetate (CH_3COONH_4) were purchased from Wako Chemical Co., Japan and IC-MA3-1 mobile phase for anion analysis was supplied by Shimadzu Co., Japan. Ultrapure water used in the photocatalytic experiments and synthesis of photocatalysts was purified using an automatic sanitation module (Millipore Co., USA). HNO₃ or NaOH was used for experimental runs requiring pH adjustment.

2.2. Synthesis and characterization of Fe and Nb co-doped photocatalyst

Fe:Nb co-doped and undoped TiO₂ (labeled as SG-TiO₂) were prepared using the temperature-controlled sol-gel process described in literature [11]. For the co-doped sample, the volume of TiO₂ precursor (titanium tetraisopropoxide) and weight of metal sources (ferric nitrate and ammonium niobium oxalate) were pre-determined to obtain a TiO₂ photocatalyst product containing 0.25 mol% Fe:Nb (1:1), labeled as Fe:Nb-TiO₂. The photocatalyst powders, including the commercially available Aeroxide TiO₂ P25 (labeled as AO-TiO₂ P25), were analyzed for their physical and chemical properties, such as X-ray diffraction (XRD) for crystal composition (MultiFlex XRD, Rigaku Co., Japan), UV-vis diffuse reflectance spectroscopy (DRS) for light absorption (JASCO ISV-722, JASCO Co., Japan), BET-N₂ adsorption isotherm for specific surface area (Autosorb-1 Analyzer, Quantachrome Instruments, USA), and SEM-EDX for surface composition (JSM-5310 SEM and JED-2140 EDX Microanalyzer, JEOL Ltd., Japan).

2.3. Photoreactor and photocatalytic experiment

The photoreactor system (Heraeus Noblelight, Germany) used in this study is equipped with a 150-W medium pressure mercury lamp (TQ 150 001725) with an emission spectrum of 200–600 nm located at the axial center of the reactor vessel. This set-up is provided with two types of water cooling circulation system: (1) quartz, which transmits of both UV and visible light; and (2) glass, which filters UV radiation under 400 nm and transmits visible light only. With the cooling tube inserted, the reactor vessel has 650 ml effective volume. For this study, the quartz cooling tube was used in the photocatalytic experiments. The photoreactor system is placed on top of a magnetic stirrer for continuous mixing of the PFOA solution-photocatalyst suspension during irradiation.

A stock solution of PFOA (400 mg L^{-1}) was prepared and kept in the refrigerator. Prior to the photocatalytic experiments, the stock solution was diluted to 0.1 mM (600 ml) which was set as PFOA initial concentration in this study. After the initial sample was taken, the photocatalyst powder was added, air was bubbled to the reaction solution in the reactor vessel and irradiation was started. Throughout the experimental run, the reaction solution was magnetically stirred continuously. Samples drawn at selected intervals from the photocatalytic experiment were pushed through a $0.45 \mu\text{m}$ syringe filter disks. Filtrates were then analyzed for PFOA concentration and decomposition by-products.

2.4. Analytical procedures

PFOA concentration in the samples was determined by liquid chromatography-mass spectrometry system (LCMS-2010EV, Shimadzu Co., Japan), along with the identification of products resulting from the photocatalytic degradation. For the chromatographic separation of sample components, ZORBAX Eclipse XDB C-18 (Agilent Technologies, USA) narrow-bore column was used with dimensions $2.1 \text{ mm} \times 50 \text{ mm}$, $3.5 \mu\text{m}$. Column oven temperature was set 40°C isothermally. The binary mobile phase was a

Table 1
Characterization data of photocatalysts.

Photocatalyst	BET surface area (m^2/g)	Crystal size (nm)	Crystal phase (w:w%)
AO-TiO ₂ P25	53.2	21.8	Anatase:rutile (84:16)
SG-TiO ₂	114.5	16.4	Anatase:rutile (90:10)
Fe:Nb-TiO ₂	120.2	11.4	Anatase (100)

solution of (A) 10 mM ammonium acetate in water, and (B) 10 mM ammonium acetate in 80:20 methanol/water. Mobile phase flow was isocratic at 70% B for the entire analysis run, at the rate of 0.2 ml min^{-1} . Injection volume was $1 \mu\text{L}$ and analysis stop time was 12 min. Mass spectrometric analysis was conducted in electrospray ionization (ESI), negative ion mode. Using the selected ion monitoring mode (SIM), PFOA concentration in the samples was quantified and the decomposition intermediates were identified.

Ion chromatography system (PIA-1000, Shimadzu Co., Japan) was used to measure the fluoride ion concentration in the samples fitted with Shim-pack IC-A3 analytical column ($2 \text{ mm ID} \times 15 \text{ cm}$). The mobile phase used was a pre-mixed solution labeled as 'IC-MA3-1 mobile phase for anion analysis'. The system is equipped with a conductivity detector and SIL-10Ai auto-injector.

3. Results and discussion

3.1. Characterization data

The physico-chemical characterization data of the photocatalysts are summarized in Table 1. Sol-gel derived photocatalysts, namely SG-TiO₂ and Fe:Nb TiO₂ have larger specific surface area than the commercially available AO-TiO₂ P25. Metal doping at a specific concentration, particularly Fe, can have a favorable effect on the surface area. However, at an excess doping concentration, it could result to the damage of the porous framework, thus negatively affecting the surface area [12].

The XRD patterns of the photocatalysts are shown in Fig. 1. The patterns show a combination of anatase and rutile phases for AO-TiO₂ P25 and SG-TiO₂ and from these patterns the weight percent of both phases were determined using the formula reported in literature [13] based on peak intensities of anatase at (1 0 1) and rutile at (1 1 0). Pure anatase phase was observed for Fe:Nb-TiO₂. While

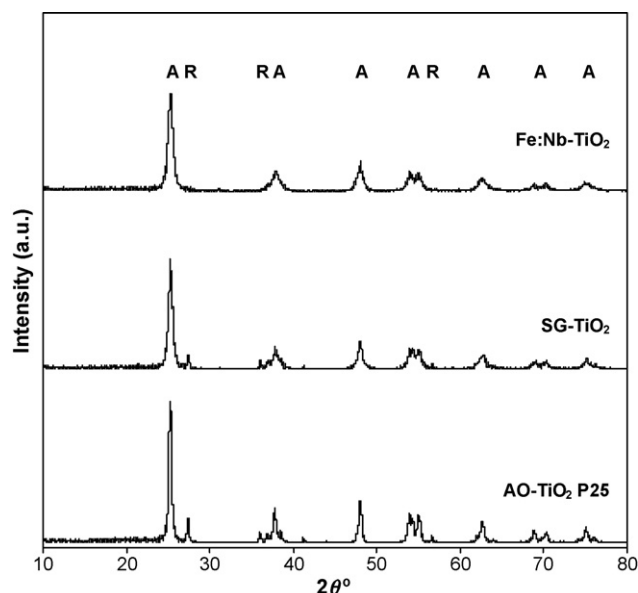


Fig. 1. XRD patterns of the photocatalysts: (A) anatase and (R) rutile.

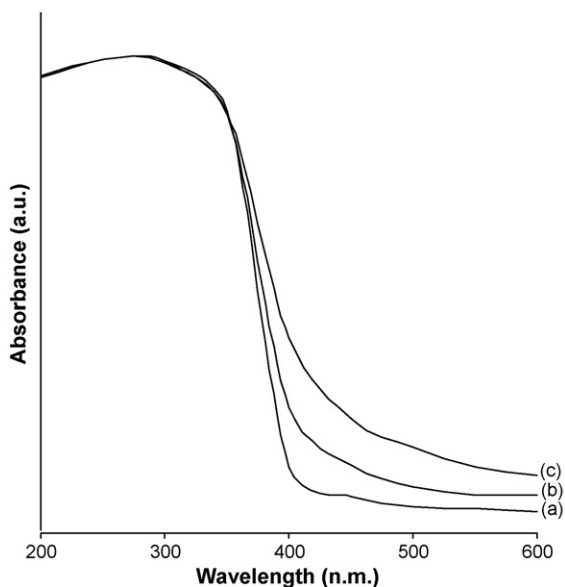


Fig. 2. UV–vis DRS of the photocatalysts: (a) AO-TiO₂ P25, (b) SG-TiO₂, and (c) Fe:Nb-TiO₂.

characteristic peaks indicating the doped metals were not detected, doping seemed to have prevented the anatase transformation to rutile, and reduced the crystallite growth with smaller crystal size obtained for Fe:Nb-TiO₂. Metals may have been finely dispersed, incorporated in the TiO₂ crystal structure, or crystals are too small for detection due to a relatively low metal loading.

The UV–vis diffuse reflectance spectra depicted in Fig. 2 show the improved absorption of Fe:Nb-TiO₂ at the visible light region ($\lambda > 400$ nm). The introduction of metals into the TiO₂ led to significant red shift. Similar observations on the effect of metal doping on visible light absorption of TiO₂ have been reported [14,15]. The red shift indicates the lowering of band gap energy of TiO₂ due to distortion caused by metals into its structure.

3.2. Photocatalytic decomposition of PFOA

The pH of PFOA solution with initial concentration of 0.1 mM was 4.3. No pH adjustment was done and all other experimental conditions were fixed to compare the decomposition efficiencies of the three photocatalysts towards PFOA decomposition. Photocatalyst loading was 0.5 g L⁻¹ for all experimental runs. The reaction solution pH was not affected by the addition of photocatalyst and the change in pH was negligible during the course of photocatalytic reaction. Under a combined UV–vis light irradiation at wavelengths ranging from 200 to 600 nm, Fe:Nb-TiO₂ photocatalyst showed the highest activity for PFOA degradation with almost twice the percentage degradation compared to that of the SG-TiO₂. In contrast, degradation using AO-TiO₂ P25 was almost insignificant. Fig. 3 shows the photocatalytic degradation profiles of PFOA using the three photocatalysts. The superior degradation efficiency of Fe:Nb-TiO₂ could be attributed to a larger surface area compared to two other photocatalysts. The specific surface area of Fe:Nb-TiO₂ is more than twice higher than that of AO-TiO₂ P25, and slightly higher than that of SG-TiO₂. Another probable factor could be the presence of rutile phase in both SG-TiO₂ and AO-TiO₂ P25, which is known to be the less photoactive type of TiO₂. In addition, the more refined crystallite size of the co-doped photocatalyst might have a positive effect on the degradation efficiency [16].

The more apparent reason for the higher activity of Fe:Nb-TiO₂ was the significant absorption shift to the visible region as shown in Fig. 2. This suggests the cooperative effects of Fe and Nb co-

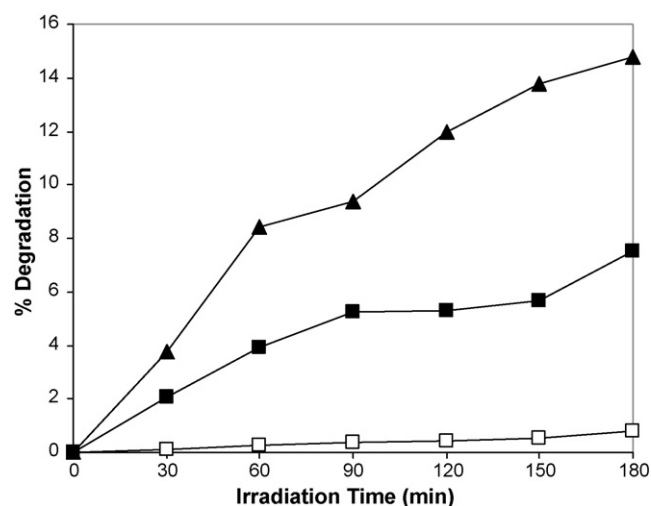


Fig. 3. Degradation profiles of PFOA using different photocatalysts: (▲) Fe:Nb-TiO₂, (■) SG-TiO₂, and (□) AO-TiO₂ P25; pH 4, C₀[PFOA] = 0.1 mM, and photocatalyst loading = 0.5 g L⁻¹.

doping on TiO₂, with Fe narrowing the band gap energy as a result of its substitution in the TiO₂ lattice, giving rise to the activation of electron–hole (e⁻/h⁺) pairs at extended wavelengths. The difference in valence states between Ti⁴⁺ and Fe³⁺ creates oxygen vacancies for charge compensation. The occurrence of oxygen vacancies, and oxygen mobility in the TiO₂ structure, were found to be beneficial to its photocatalytic activity [17]. Nb, on the other hand, being present on the TiO₂ surface, as detected in SEM-EDX as shown in Fig. 4, emerged to trap the migrated electrons (e⁻), leaving the holes (h⁺) free to react with H₂O molecules to form hydroxyl radicals (*OH), which in turn could have degraded the PFOA molecules and prevented the rapid recombination with electrons. The location of metal dopants is an important factor affecting the activity of photocatalyst, whether metal species are substituted in the position of Ti⁴⁺ in the TiO₂ lattice or dispersed on its surface [18]. While hydroxyl radical (*OH) has been known to decompose a wide range of halogenated organic compounds, the main mechanism of reaction is via hydrogen abstraction to form water. But in the case of PFOA, all hydrogen molecules have been replaced by fluorine in the carbon chain. This fluorine substitution for organic hydrogen in PFOA molecule made it inert from *OH radical attack [19], thus reaction with h⁺ upon adsorption is seen to be the dominant reaction for PFOA decomposition. The photo-

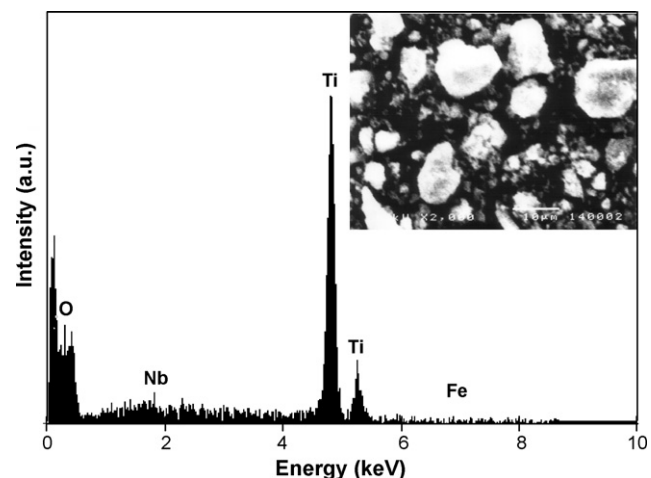


Fig. 4. Elemental EDX profile of Fe:Nb-TiO₂, inset: SEM micrograph.

generated holes (h^+) are also known to be reactive species [20] which can initiate electron transfer from the adsorbed perfluorocarboxylate anion on TiO_2 surface leading to subsequent reactions yielding shorter carbon chain PFCAs, CO_2 and fluoride ions. A two-step PFCa degradation reaction had been proposed [7] with the initial step involving the electron transfer from the adsorbed perfluorocarboxylate anion to the valence band hole of TiO_2 , followed by a release of CO_2 from the terminal carboxylate group forming perfluoroalkyl radical. Molecular dissolved oxygen reacts with the perfluoroalkyl radical to form peroxy radical which is converted into PFCa shortened by one CF_2 -unit, thus releasing two fluoride ions. In a photocatalytic system using undoped TiO_2 , O_2 is required as acceptor of electron generated upon light absorption. With Fe:Nb co-doped TiO_2 , this role of O_2 could have been assumed by one of the dopant metals, most probably Nb being present on the TiO_2 surface, leading O_2 to function solely as a reactant to perfluoroalkyl radical. The seemingly absent competition reaction (as electron acceptor) for O_2 could substantiate the much superior activity of the Fe:Nb co-doped TiO_2 compared to the undoped powder and the commercially available material.

Photocatalytic degradation by TiO_2 is defined by its surface properties, which are closely dependent on the solution pH where it is applied. Photocatalytic degradation experiments of PFOA in the presence of Fe:Nb- TiO_2 photocatalyst at pH 4, 7 and 9 were conducted to determine the influence of the pH on PFOA decomposition. At pH 4, which is the inherent pH of 0.1 mM PFOA, the highest degradation was observed. This can be attributed to the electrostatic attraction between the negatively charged perfluorooctanoate ion and the positively charged TiO_2 surface, promoting surface reaction with the valence band holes (h^+). At pH 6–7, TiO_2 has a neutral or zero point charge and exists in the solution as $Ti-OH$. TiO_2 assumes the $Ti-OH_2^+$ form in acidic solution; while in alkaline conditions it is present in the form of TiO^- [8]. TiO_2 doped with 0.3 mol% of Fe had been reported to have a point of zero charge (pzc) of 7.2 [23]. On the part of PFOA, it has a pK_a value of 2.8 [21] which indicates that in water, it is mostly present in dissociated form as perfluorooctanoate anion. Valence band holes (h^+) of TiO_2 could have played an important role in the degradation PFOA in acidic pH, as it is noted that its oxidative power is also pH dependent and increases as the pH decreases [7]. However, due to the exceptional stability of PFOA, it was not fully mineralized but degraded into shorter carbon perfluorocarboxylic acids, with fluoride ions simultaneously released as photocatalytic reaction intermediates and products.

3.3. Reaction intermediates and defluorination

As a result of the incomplete mineralization of PFOA ($C_7F_{15}COOH$; $m/z=413$), perfluorinated carboxylic acids (PFCAs) with shorter carbon chain were detected by LC/MS. Among these PFCAs are perfluoroheptanoic acid ($C_6F_{13}COOH$; $m/z=363$), perfluorohexanoic acid ($C_5F_{11}COOH$; $m/z=313$), perfluoropentanoic acid (C_4F_9COOH ; $m/z=263$), and perfluorobutanoic acid (C_3F_7COOH ; $m/z=213$). A typical total ion chromatogram (TIC) of PFOA and its decomposition intermediates is shown in Fig. 5. As the concentration of PFOA decreased with irradiation time, a corresponding increase in the peak areas of the reaction intermediates was observed, notably for perfluoroheptanoic acid and perfluorohexanoic acid. The reaction intermediate with the shortest carbon chain, perfluorobutanoic acid, was detected only after 180 min of irradiation.

This observation suggests that PFOA was decomposed in a step-wise manner, starting with the formation of longer PFCAs (e.g. perfluoroheptanoic acid), which were subsequently oxidized further to shorter PFCAs (e.g. perfluorobutanoic acid) at extended reaction time. This step-wise decomposition indicates the detach-

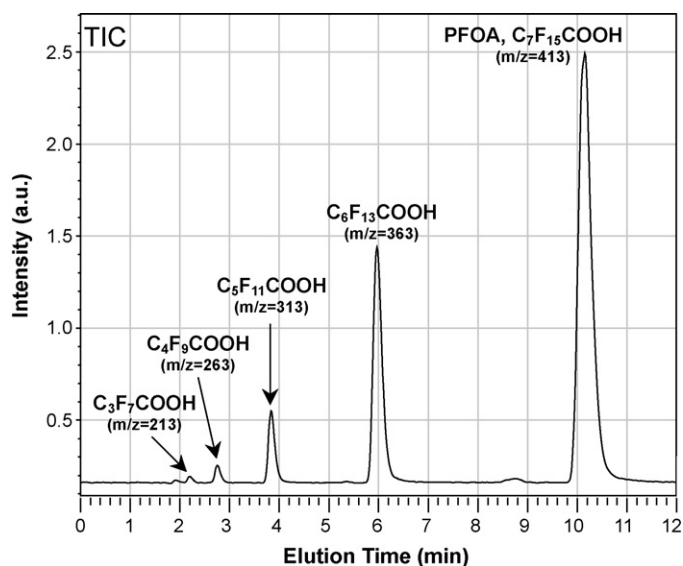


Fig. 5. Total ion chromatogram (TIC) of PFOA after 180 min of irradiation in the presence of Fe:Nb- TiO_2 , pH 4, $C_0[PFOA]=0.1$ mM, Fe:Nb- TiO_2 loading = 0.5 g L^{-1} .

ment of CF_2 unit to form CO_2 (decarboxylation) and fluoride ions. The irradiation time-dependent plot of the peak areas of PFOA and its reaction intermediates is illustrated in Fig. 6.

Although fluoride ions were detected in the aqueous samples, the concentrations were much lower than expected, as $15 F^-$ ions are to be generated for every molecule of PFOA decomposed. Fluoride ions may have adsorbed on the photocatalyst surface as pH of the sample solution remained in the acidic range (4.3–4.6) during the reaction. At acidic pH, TiO_2 surface is positively charged [22], making adsorption of fluoride ions probable resulting to very low concentrations in the aqueous phase. Complete decomposition of PFOA was hardly achieved, which could provide a plausible explanation for the low concentrations of F^- ions in the sample solution, as fluorines remained attached to the shorter carbon chain PFCAs. For photocatalytic experiments conducted at higher pH (7 and 9), F^- ion concentrations were below the detection limit of the ion chromatograph, mainly due to the low percentage degradations recorded for these experimental runs.

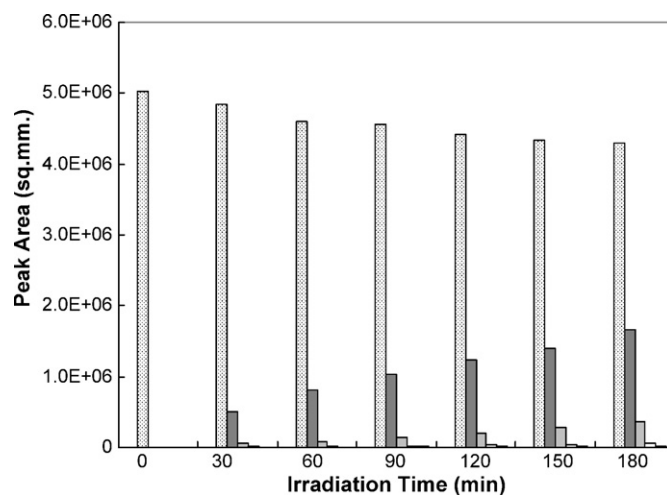


Fig. 6. Time-dependent plot of PFOA degradation and formation of reaction intermediates using Fe:Nb- TiO_2 photocatalyst: PFOA, $C_6F_{13}COOH$, $C_5F_{11}COOH$, C_4F_9COOH , and C_3F_7COOH . pH 4, $C_0[PFOA]=0.1$ mM, Fe:Nb- TiO_2 loading = 0.5 g L^{-1} .

4. Conclusions

TiO₂ co-doped with Fe and Nb (Fe:Nb-TiO₂) prepared by sol-gel method had been applied to the photocatalytic decomposition of perfluorooctanoic acid (PFOA) in aqueous solution and showed a superior activity compared to that pure TiO₂ synthesized using the same method (SG-TiO₂) and that of the commercially available TiO₂ photocatalyst, Aeroxide TiO₂ P25 (AO-TiO₂ P25). Metal co-doping was seen beneficial in terms of enhancing the physico-chemical properties of TiO₂ such as specific surface area, crystallite size, visible light absorption, and prevented the anatase transformation to rutile. These were found favorable for the photocatalytic degradation of PFOA. More importantly, the higher activity of Fe:Nb-TiO₂ could be attributed to the cooperative effects of the metals, with Fe lowering the band gap energy, and Nb functioning as electron trap and prevented the recombination of electron-hole pairs, consequently promoted the higher absorbance at extended wavelengths and enhanced the charge separation. As a result of photocatalytic decomposition of PFOA, perfluorocarboxylic acids with shorter carbon chain lengths along with fluoride ions were detected as reaction intermediates and products. It is recommended for further study the kinetic analysis of the reactions involved including the determination of rate constants, formation rate of products, as well as the investigation of physico-chemical properties of Fe:Nb-TiO₂ which are deemed crucial to photo-activity such as point of zero charge (zpc) and recombination rate of excited electrons and holes.

References

- [1] K. Prevedouros, I.T. Cousins, R.C. Buck, S.H. Korzeniewski, Sources, fate and transport of perfluorocarboxylates, *Environ. Sci. Technol.* 40 (2006) 32–44.
- [2] T.J. Wallington, M.D. Hurley, J. Xia, D.J. Wuebbles, S. Sillman, J. Martin, S.A. Mabury, O.J. Nielsen, M.P. Sulbaek Andersen, Formation of C₇F₁₅COOH (PFOA) and other perfluorocarboxylic acids during the atmospheric oxidation of 8:2 fluorotelomer alcohol, *Environ. Sci. Technol.* 40 (2006) 924–930.
- [3] P.M. Hinderliter, M.P. DeLorme, G.L. Kennedy, Perfluorooctanoic acid: relationship between repeated inhalation exposures and plasma PFOA concentration in the rat, *Toxicology* 222 (2006) 80–85.
- [4] C. Potera, Reproductive toxicology: study associates PFOS and PFOA with impaired fertility, *Environ. Health Perspect.* 117 (2009) A148.
- [5] H. Hori, E. Hayakawa, K. Koike, H. Einaga, T. Ibusuki, Decomposition of non-fluoropentanoic acid by heteropolyacid photocatalyst H₃PW₁₂O₄₀ in aqueous solution, *J. Mol. Catal. A: Chem.* 211 (2004) 35–41.
- [6] S. Kutsuna, H. Hori, Rate constants for aqueous-phase reactions of SO₄⁻ with C₂H₅C(O)O⁻ at 298 K, *Int. J. Chem. Kinet.* 39 (2007) 276–288.
- [7] R. Dillert, D. Bahnemann, H. Hidaka, Light-induced degradation of perfluorocarboxylic acids in the presence of titanium dioxide, *Chemosphere* 67 (2007) 785–792.
- [8] S.C. Panchangam, A.Y.C. Lin, J.H. Tsai, C.F. Lin, Sonication-assisted photocatalytic decomposition of perfluorooctanoic acid, *Chemosphere* 75 (2009) 654–660.
- [9] K. Marouf-Khelifa, F. Abdelmalek, A. Khelifa, A. Addou, TiO₂-assisted degradation of perfluorinated surfactant in aqueous solutions treated by gliding arc discharge, *Chemosphere* 70 (2008) 1995–2001.
- [10] L. Ravichandran, K. Selvam, B. Krishnakumar, M. Swaminathan, Photovalorization of pentafluorobenzoic acid with platinum doped TiO₂, *J. Hazard. Mater.* 167 (2009) 763–769.
- [11] C.R. Estrellan, C. Salim, H. Hinode, Photocatalytic activity of sol-gel derived TiO₂ co-doped with iron and niobium, *React. Kinet. Catal. Lett.* 98 (2009) 187–192.
- [12] H. Hao, J. Zhang, The study of iron (III) and nitrogen co-doped mesoporous TiO₂ photocatalysts: synthesis, characterization and activity, *Micropor. Mesopor. Mater.* 121 (2009) 52–57.
- [13] H. Zhang, J.F. Banfield, Understanding polymorphic phase transformation behavior during growth of nanocrystalline aggregates: insights from TiO₂, *J. Phys. Chem. B* 104 (2000) 3481–3487.
- [14] Z. Wang, C. Chen, F. Wu, B. Zou, J. Meng Zhao, C. Wang, Feng, Photodegradation of rhodamine B under visible light by bimetal co-doped TiO₂ nanocrystals, *J. Hazard. Mater.* 164 (2009) 615–620.
- [15] P. Vijayan, C. Mahendiran, C. Suresh, K. Shanthi, Photocatalytic activity of iron doped nanocrystalline titania for the oxidative degradation of 2,4,6-trichlorophenol, *Catal. Today* 141 (2009) 220–224.
- [16] J.-W. Shi, J.T. Zhang, Y. Hu, Y.-C. Zhao, Influence of Fe³⁺ and Ho³⁺ co-doping on the photocatalytic activity of TiO₂, *Mater. Chem. Phys.* 106 (2007) 247–249.
- [17] A.A. Ismail, M. Abboudi, P. Holloway, Photoluminescence from terbium doped silica-titania prepared by a sol-gel method, *Mater. Res. Bull.* 42 (2007) 137–142.
- [18] S.S. Srinivasan, J. Wade, E.K. Stefanakos, Y. Goswami, Synergistic effects of sulfation and co-doping on the visible light photocatalysis of TiO₂, *J. Alloys Compd.* 424 (2006) 322–326.
- [19] H.F. Schroder, R.J.W. Meesters, Stability of fluorinated surfactants in advanced oxidation processes—a follow up of degradation products using flow injection-mass spectrometry, liquid chromatography-mass spectrometry and liquid chromatography-multiple stage mass spectrometry, *J. Chromatogr.* 1082 (2005) 110–119.
- [20] D.W. Bahnemann, M. Hilgendorff, R. Memming, Charge carrier dynamics at TiO₂ particles: reactivity of free and trapped holes, *J. Phys. Chem. B* 101 (1997) 4265–4275.
- [21] K.U. Goss, The pK_a values of PFOA and other highly fluorinated carboxylic acids, *Environ. Sci. Technol.* 42 (2008) 456–458.
- [22] N. Spanos, I. Georgiadou, A. Lycourghiotis, Investigation of rutile, anatase, and industrial titania/water solution interfaces using potentiometric titration and microelectrophoresis, *J. Colloid Interface Sci.* 172 (1995) 374–382.
- [23] A. Di Paola, S. Ikeda, G. Marci, B. Ohtani, L. Palmisano, Transition metal doped TiO₂: physical properties and photocatalytic behaviour, *Int. J. Photoenergy* 3 (2001) 171–176.