

# **Developing efficient photocatalysts for high-performance decomposition of perfluorooctanoic acid**

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Thesis submitted in fulfilment of the requirements for  
the degree of

**Doctor of Philosophy**

under the supervision of Prof. Bing-Jie Ni

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# CERTIFICATION OF ORIGINAL AUTHORSHIP

I, Xiaoqing Liu declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Civil and Environmental Engineering/Faculty of Engineering and Information Technology at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literatures used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

This research is supported by the Australian Government Research Training Program.

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## RESEARCH PUBLICATIONS

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## LIST OF ABBREVIATIONS

<b>Symbol</b>	<b>Description</b>
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFPeA	Perfluoropentanoic acid
PFBA	Perfluorobutanoic acid
PFPA	Pentafluoropropionic acid
TFA	Trifluoroacetic acid
PFCAs	Perfluorocarboxylic acids
MOFs	Metal-organic frameworks
In-BDC	Indium (III)-benzenedicarboxylate
PFCs	Perfluorinated chemicals
PFECAs	Perfluoroalkyl ether carboxylic acids
PFAS	Perfluoroalkyl substances
DMF	N,N-dimethylformamide
NS	Nanosphere
SEM	Scanning electron microscopy
XRD	X-ray diffraction
ITO	Indium tin oxide
XPS	X-ray photoelectron spectroscopy
SSA	Specific surface areas
TEM	Transmission electron microscopy
ESR	Electron spin resonance
PL	Photoluminescence spectroscopy
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
FTIR	Fourier transform infrared
EIS	Electrochemical impedance spectroscopy
UHPLC-MS/MS	Triple quadrupole ultra-high-performance liquid chromatograph tandem mass spectrometer
MRM	Multiple reaction monitoring

SI	Supporting Information
BJH	Barrett-Joyner-Halenda
BET	Brunauer-Emmett-Teller
BE	Binding energy
O <sub>v</sub>	Oxygen vacancy
EIS	Electrochemical impedance spectroscopy
TOC	Total organic carbon
DMPO	5,5-dimethyl-1-pyrroline-N-oxide
TG	Thermogravimetric
MCT	Mercury cadmium telluride
VB	Valence band
CB	Conduction band
BIEF	Built-in electric field
IEF	Internal electric field
BiOX	Bismuth oxyhalide
KX	Potassium halide
BQ	p-benzoquinone
BTA	Tertbutyl alcohol
ROS	Reactive oxygen species
IPA	Isopropanol
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl free radical
SACs	Single atom catalysts
SPR	Surface plasmon resonance
HAADF	High angle annular dark field
STEM	Scanning transmission electron microscopy

## LIST OF SYMBOLS

Symbol	Description
KI	Potassium iodide
C <sub>7</sub> F <sub>15</sub> COOH	Perfluorooctanoic acid
C <sub>6</sub> F <sub>13</sub> COOH	Perfluoroheptanoic acid
C <sub>5</sub> F <sub>11</sub> COOH	Perfluorohexanoic acid
C <sub>4</sub> F <sub>9</sub> COOH	Perfluoropentanoic acid
C <sub>3</sub> F <sub>7</sub> COOH	Perfluorobutanoic acid
C <sub>2</sub> F <sub>5</sub> COOH	Pentafluoropropionic acid
CF <sub>3</sub> COOH	Trifluoroacetic acid
e <sub>cb</sub> <sup>-</sup>	Photo-induced electron
NaOAc	Sodium acetate
In(OH) <sub>3</sub>	Indium hydroxide
<i>E<sub>g</sub></i>	Band gap
F <sup>-</sup>	Fluoride ion
In <sub>2</sub> O <sub>3</sub>	Indium oxide
TiO <sub>2</sub>	Titanium dioxide
Ga <sub>2</sub> O <sub>3</sub>	Gallium oxide
Na <sub>2</sub> SO <sub>4</sub>	Sodium sulfate
•OH	Hydroxyl radical
O <sub>2</sub> <sup>•-</sup>	Superoxide radical
t-BuOH	t-butyl alcohol
FeCl <sub>3</sub>	Ferric chloride anhydrous
Fe <sup>3+</sup>	Ferric ion
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Sodium oxalate
λ <sub>g</sub>	Band gap wavelength



## Ph.D. DISSERTATION ABSTRACT

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**Thesis title:** Developing efficient photocatalysts for high-performance decomposition of perfluorooctanoic acid

**Faculty:** Faculty of Environmental and Information Technology

**School:** Civil and Environmental Engineering

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### Abstract

Perfluorochemicals (PFCs) are a set of chemicals containing C-F bonds, which are concerned due to their persistent and toxicological properties. Perfluorooctanoic acid (PFOA,  $C_7F_{15}COOH$ ) is one of the most widely used PFCs. Photocatalytic approaches appear to be an effective way for the removal of PFCs. We first used metal-organic frameworks (MOFs) derived  $In_2O_3$  for photocatalytic degradation of PFOA under UV light irradiation. The results show that PFOA was completely decomposed in 3 h. MOFs-derived  $In_2O_3$  was super-hydrophilic with a contact angle of  $\sim 20^\circ$ , which facilitated the tight coordination between PFOA and  $In_2O_3$ .

Lower calcination temperatures enable higher oxygen vacancy concentrations and larger specific surface area (SSA) of  $In_2O_3$ .  $In_2O_3$  prepared at 300 °C ( $In_2O_3$ -300) and 400 °C ( $In_2O_3$ -400) demonstrated better catalytic performance, and PFOA ( $10\text{ mg L}^{-1}$ ) could be completely removed within 4 h, with a defluorination ratio of 39% over  $In_2O_3$ -400 in 8h.  $Fe^{3+}$  only slightly increased the defluorination ratio of PFOA over  $In_2O_3$ -400 to 43%. A much higher defluorination ratio of  $\sim 60\%$  was obtained in  $In_2O_3$ -600 system

after the addition of  $\text{Fe}^{3+}$ , than the defluorination ratio of  $\sim 20\%$  over  $\text{In}_2\text{O}_3$ -600. Combined with a series of characterizations, we speculated that  $\text{Fe}^{3+}$  participated in the coordination between PFOA and  $\text{In}_2\text{O}_3$ -600, thus promoting the defluorination of PFOA.

The  $\text{BiOX}/\text{TiO}_2$  heterojunctions demonstrated significantly enhanced efficiency for photocatalytic decomposition of perfluorooctanoic acid (PFOA) compared with  $\text{BiOX}$  or  $\text{TiO}_2$ . PFOA ( $10 \text{ mg L}^{-1}$ ) was completely degraded by  $\text{BiOCl}/\text{TiO}_2$  in 8h with a high defluorination ratio of 82 %. The charge transfer and photo-induced electron hole separation were facilitated by the p-n heterojunctions between  $\text{BiOX}$  and  $\text{TiO}_2$  and the inner electric fields (IEF) in  $\text{BiOX}$ . XRD and TEM characterizations indicated that  $\text{TiO}_2$  combined with  $\text{BiOX}$  along the [110] facet, which facilitated photo-induced electron transfer in the [001] direction, thus benefiting PFOA decomposition.

Single bismuth (Bi) atoms decorated  $\text{TiO}_2$  catalyst ( $\text{N-Bi}/\text{TiO}_2$ ) was synthesized by a green and simple UV irradiation method using  $\text{Bi}(\text{NO}_3)_3$  as the precursor. When  $\text{BiCl}_3$  was used as the Bi precursor,  $\text{BiOCl}$  nanocluster were formed on the surface of  $\text{TiO}_2$  (denoted as  $\text{Cl-Bi}/\text{TiO}_2$ ). Both  $\text{N-Bi}/\text{TiO}_2$  and  $\text{Cl-Bi}/\text{TiO}_2$  demonstrated excellent performance for the defluorination of PFOA. In-situ DRIFTS spectra demonstrated that the Bi single atoms in  $\text{N-Bi}/\text{TiO}_2$  induced the ionization of C-F bond of PFOA, leading to the deep defluorination of PFOA. Our findings provide approaches for manipulating the photocatalytic activities of  $\text{In}_2\text{O}_3$  and  $\text{TiO}_2$ -based composites for the high-performance decomposition of PFOA.

**Keywords:** Metal-organic frameworks; hydrophilic  $\text{In}_2\text{O}_3$ ;  $\text{In}_2\text{O}_3$ ; perfluorooctanoic acid; photocatalytic degradation; oxygen vacancies;  $\text{Fe}^{3+}$ ; defluorination ratio; inner electric fields; band alignment; Bi single atoms; in-situ DRIFTS.