

ELECTRONIC SUPPLEMENTARY INFORMATION

Unlocking the Effect of Zn²⁺ on Crystal Structure, Optical Properties, and Photocatalytic Degradation of Perfluoroalkyl Substances (PFAS) of Bi₂WO₆

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LC-QTOF/MS – instrumentation and analysis conditions

A 1200 Series high-performance liquid chromatograph (Agilent Technologies) fitted with autosampler, quaternary pump with degasser, column thermostat and coupled to a tandem mass spectrometer (Agilent Technologies 6538 UHD Accurate Mass Q-TOF LC/MS) equipped with a dual ESI ion source was used. The analytical column used was the Zorbax Eclipse Plus C18 rapid resolution HT (2.1×50 mm, $1.8 \mu\text{m}$). A 3-min linear gradient of aqueous solutions ($5 \text{ mmol}\cdot\text{L}^{-1}$) of ammonium formate (A) and methanol (B) with an increase from 30% to 60% (3 min post-run at 30% B, $0.3 \text{ mL}\cdot\text{min}^{-1}$ flow rate, and 40°C column temperature) was used in the chromatographic analyses. The analytes were ionized in the negative ion polarity mode. The temperature of an ion source gas (nitrogen) was 280°C , and the flow rate was $9 \text{ L}\cdot\text{min}^{-1}$. The capillary potential, fragmentor, and nebulizer pressure were set to 3500 V, 80 V, and 35 psi, respectively. The ions were acquired in a MS scan mode at 50-1000 m/z with a scan rate of 1 scan s^{-1} (number of transients: 5975 and collision energy: 0 eV). Internal mass calibration was enabled using three reference mass ions (112.985587, 301.998139, and 1033.988109). The samples were analyzed in triplicate (injection volume: $5 \mu\text{L}$). After the sample injection, the needle was washed with methanol. The quantification was performed on unprotonated ions $[\text{M-H}]^-$. For PFH_xA , an ion of $m/z = 312.9748$ and the isotopically labeled internal standard ($^{13}\text{C}_6$ - PFH_xA) ion of $m/z = 318.9921$ were extracted, respectively. Data acquisition and analysis were performed using Agilent Mass Hunter software versions B.06.01 and B.07.00, respectively. For the quantitative analysis of PFH_xA , each sample was fortified with $^{13}\text{C}_6$ - PFH_xA ($0.25 \text{ mg}\cdot\text{L}^{-1}$), vortexed, and passed through a $0.22 \mu\text{m}$ polypropylene (PP) syringe filter (Bioanalytic, Gdańsk, Poland) into the PP chromatographic vial and analyzed using LC-QTOF/MS. An example of the extracted ion chromatograms is presented in Figure S1.

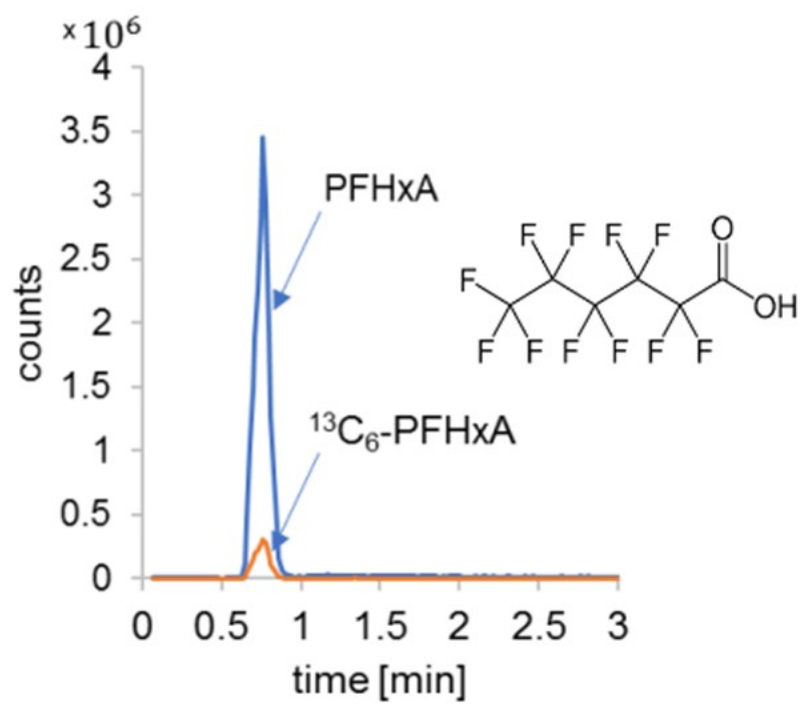


Figure S1. Extracted ion chromatograms of PFH_xA and $^{13}\text{C}_6$ -PFH_xA.

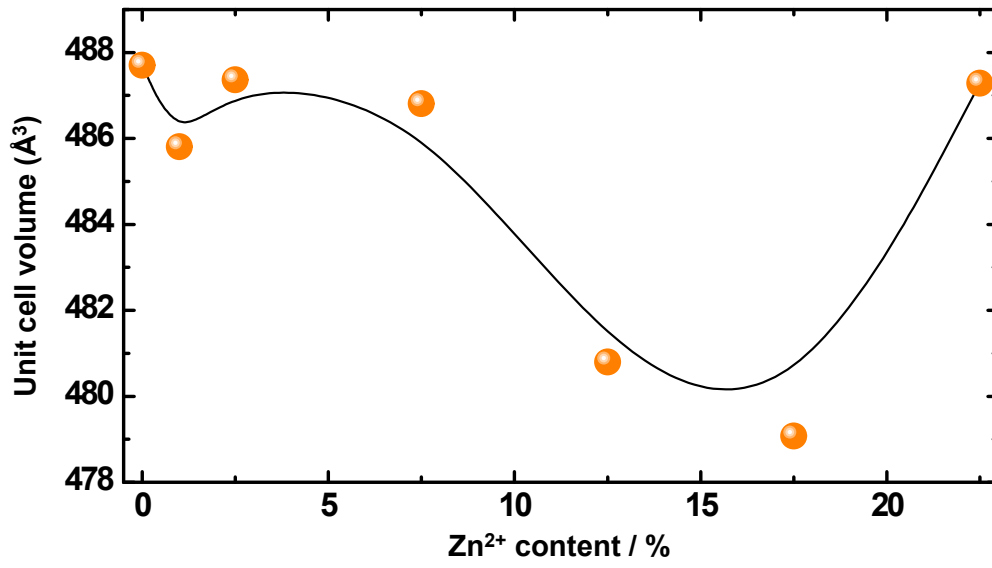


Figure S2. Unit cell volume of $\text{Bi}_{2-x}\text{Zn}_x\text{WO}_{6+\delta}$ as a function of Zn^{2+} content.

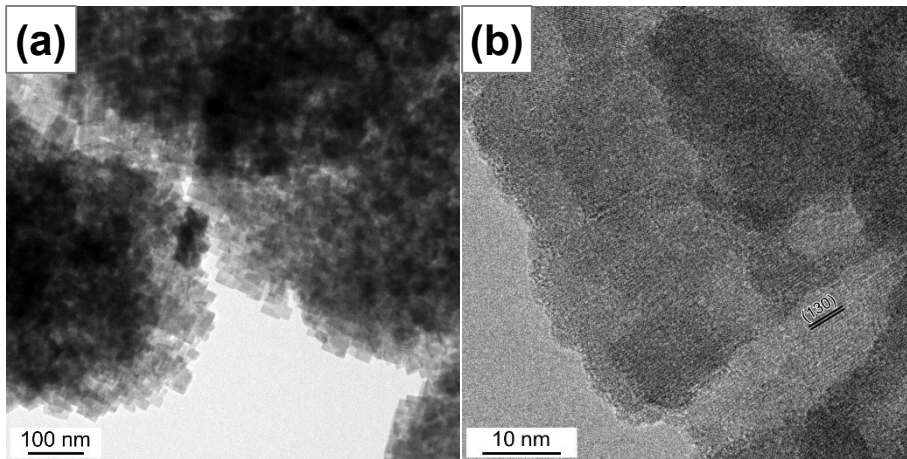


Figure S3. TEM (a) and HRTEM (b) images of Zn_{17.5}.

Table S1. Comparative results of PFAS degradation.

Conditions	Efficiency	Light source	References
Photo-Fenton process	90% degradation and 53.2% defluorination after 5 h	UV	<i>Chem. Eng. J.</i> , 2012, 184 , 156–162.
In ₂ O ₃ porous nanospheres	100% within 30 min	UV	<i>Appl. Catal. B</i> , 2012, 125 , 350–357.
BiOCl	59.3% defluorination after 3 h	UV	<i>Chem. Eng. J.</i> , 2017, 317 , 925–934.
β -Ga ₂ O ₃ nanoplates	100% within 3 h	UV (185 nm)	<i>Appl. Catal. B</i> , 2013, 142–143 , 654–661.
In ₂ O ₃	100% decomposition of PFAS	UV	<i>Chemosphere</i> , 2017, 189 , 717–729.
Fe/TNTs@AC	>90% decomposition of PFOA in 4 h, of which 62% was completely mineralized to F ⁻	UV	<i>Water Res.</i> , 2020, 185 , 116219.
Iron nanoparticles (Fe ⁰)	90±1% degradation after 2 h	UV (pH=3.0)	<i>J. Water Process. Eng.</i> , 2022, 46 , 102556.
WO ₃ /TiO ₂ catalysts (0–5 wt% WO ₃)	4 %–26 % after 4 h	UVA+Vis+O ₃	<i>Sci. Total Environ.</i> , 2022, 843 , 157006.
Pb-doped TiO ₂ coated with reduced graphene oxide	98% after 24 h	UV	<i>Water Environ. Res.</i> , 2023, 95 , e10871.
Hexagonal boron nitride in UVC/VUV system	>99% degradation of PFOA in 15 min and 65% degradation of PFOS in 1 h	UVC (254 nm)	<i>Environ. Sci. Technol. Lett.</i> , 2023, 10 , 705–710.
Zn _{2.5} -Bi ₂ WO ₆	57% degradation in 45 min	Visible	This study