



# Ultraviolet irradiation-induced substitution of fluorine with hydroxyl radical for mass spectrometric analysis of perfluorooctane sulfonyl fluoride



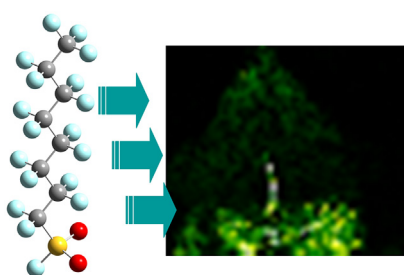
Peng Wang, Xuemei Tang, Lulu Huang, Jie Kang, Hongying Zhong\*

Mass Spectrometry Center for Structural Identification of Biological Molecules and Precision Medicine, Key Laboratory of Pesticides and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan, Hubei 430079, PR China

## HIGHLIGHTS

- Ultraviolet irradiation on semiconductor nanoparticles produces electron–hole pairs.
- Hole oxidization results in the formation of hydroxyl radicals.
- Fluorine atoms of PFOSF can be specifically substituted with hydroxyl radicals.
- Capture of photoelectrons causes dissociation and fragmentation.
- Fragments are detected in negative ion mode.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A rapid and solvent free substitution reaction of a fluorine atom in perfluorooctane sulfonyl fluoride (PFOSF) with a hydroxyl radical is reported. Under irradiation of ultraviolet laser on semiconductor nanoparticles or metal surfaces, hydroxyl radicals can be generated through hole oxidization. Among all fluorine atoms of PFOSF, highly active hydroxyl radicals specifically substitute the fluorine of sulfonyl fluoride functional group. Resultant perfluorooctane sulfonic acid is further ionized through capture of photo-generated electrons that switch the neutral molecules to negatively charged odd electron hypervalent ions. The unpaired electron subsequently initiates  $\alpha$  O–H bond cleavage and produces perfluorooctane sulfonate negative ions. Hydroxyl radical substitution and molecular dissociation of PFOSF have been confirmed by masses with high accuracy and resolution. It has been applied to direct mass spectrometric imaging of PFOSF adsorbed on surfaces of plant leaves.

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## 1. Introduction

Perfluorooctane sulfonyl fluoride (PFOSF) has been widely used in industry for production of polymers, surfactants, textile coating, stain repellent and other materials [1–3]. Because perfluorinated

compounds are not only capable of long-range transportation but also extremely resistant to environmental and biological breakdown, these synthetic chemicals were found to be ubiquitous and globally prevalent in the worldwide environments including soil, water, air as well as wildlife and human, even in remote Arctic areas [4–8]. Although PFOSF has been listed as a new POP (persistent organic pollutant), its quantitative determination is still technically challenging [9,10].

Analytical approaches involving chromatography or mass

\* Corresponding author.

E-mail address: [hyzhong@mail.cnu.edu.cn](mailto:hyzhong@mail.cnu.edu.cn) (H. Zhong).

spectrometry usually require chromophores for optical detection or ionizable functional groups for mass spectrometric detection in either positive or negative ion mode. Unfortunately, PFOSF has none of these properties [11]. Cai et al. reported a chemical derivatization method for LC-MS analysis of PFOSF with benzylamine [12] and the absolute detection limit in positive ion mode can be down to pg level. So far, no successful methods without wet chemical derivatization have been reported for rapid and quantitative determination of PFOSF. In the present work we show that substitution of fluorine with photo-generated hydroxyl radicals can instantly occur. We have proposed a mechanism that hydroxyl radicals can be generated through laser irradiation on surfaces of semiconductors or metal substrates. Then resultant perfluorooctane sulfonic acids can be ionized by capturing photo-generated electrons that switch neutral molecules to negative hypervalent ions with odd electrons. Unpaired electrons further initiate  $\alpha$ -O-H bond cleavage [13–15], resulting in the formation of negatively charged perfluorooctane sulfonate (PFOS) ions. Mass spectrometric detection of PFOSF was then achieved by measuring perfluorooctane sulfonate (PFOS) in negative ion mode with a laser desorption ionization mass spectrometer. It has been applied to the mass spectrometric imaging of PFOSF adsorbed on surfaces of plant leaves.

## 2. Experimental

### 2.1. Instrumentation

Ultraviolet irradiation-induced substitution reactions have been performed on semiconductor nanoparticles and metal substrates with a Waters SYNAPT G2 MALDI (Billerica, MA, USA) mass spectrometer. After nanoparticles spotted on the sample plate were air dried, 1  $\mu$ L solutions of standard PFOSF or samples were deposited on the surface of nanoparticles for downstream mass spectrometric analysis. These solutions can also be deposited on metal substrates. The mass spectrometer was operated in the negative ion mode. It is equipped with an Nd: YAG high repetition laser head (355 nm) and laser pulse width is 3 ns. Laser fire rate was set as 200 Hz with 100  $\mu$ J/200 Hz pulse energy. Potential difference between the sample plate and the aperture were set as 20 V. Voltages on the sample plate and aperture are 87 V and 107 V respectively for routine analysis. In negative ion mode, the instrument was calibrated with standard solution of fatty acids (including C4:0, C6:0, C8:0, C10:0, C12:0, C14:0, C16:0, C18:0, C20:0 and C22:0). Standard solution of PFOS was spotted in the lock mass well for internal calibration. Fragment ions of MS/MS experiments were also internally calibrated with the mixture of free fatty acids (C4:0-C20:0).

### 2.2. Reagents and apparatus

LC-MS grade water, acetonitrile, methanol and isopropyl alcohol were purchased from Fisher Scientific (Bridgewater, NJ, USA). Nanoparticles of bismuth cobalt zinc oxide ( $(\text{Bi}_2\text{O}_3)_{0.07}(\text{CoO})_{0.03}(\text{ZnO})_{0.9}$  (<100 nm BET or <50 nm XRD), boron nitride, zinc oxide, titanium dioxide were purchased from Sigma-Aldrich (St. Louis, MO, USA). Stainless steel plates were made by Waters (Billerica, MA, USA). Copper films were purchased from Junke (Shanghai, China). Platinum films were purchased from Gaoss Union (Wuhan, China). Mass spectrometer was calibrated with standard fatty acids (including C4:0, C6:0, C8:0, C10:0, C12:0, C14:0, C16:0, C18:0, C20:0 and C22:0) that were purchased from NuChekPrep Inc (Elysian, MN, USA). Standard perfluorooctane sulfonyl fluoride (PFOSF) and potassium perfluorooctane sulfonate were purchased from Dr. Ehrenstorfer GmbH (Bgm, Schlosser, Germany).

### 2.3. Experimental procedures

#### 2.3.1. Preparation of different substrates for photocatalytic substitution reactions

The ultraviolet irradiation induced substitution reactions have been performed on two kinds of substrates: (1) Semiconductor nanoparticles. (2) Metal substrates. Nanoparticles have been thermally treated at 350 °C for 2 h in a muffle furnace made by Jianli Furnace Co. Ltd (Yingshan, Hubei, China) before use in order to remove trace organic contaminants. Different nanoparticles including zinc oxide, titanium dioxide, bismuth cobalt zinc oxide ( $(\text{Bi}_2\text{O}_3)_{0.07}(\text{CoO})_{0.03}(\text{ZnO})_{0.9}$ ) and boron nitride have been suspended in solutions of isopropyl alcohol (10 mg/mL) respectively. They were spotted on surfaces of sample plates for downstream analysis. Laser activated electron tunneling has also been examined on surfaces of stainless steel sample plate, or copper and platinum films. These metal films were tightly stuck to the sample plate after polishing.

#### 2.3.2. Density functional theory (DFT) studies of perfluorooctane sulfonyl fluoride (PFOSF) and perfluorooctane sulfonic acid (PFOS)

In order to understand the mechanisms of bond cleavages and new bond formation, DFT was used as a quantum mechanical modeling method to investigate the electronic structures of PFOSF and PFOS. Ground state electronic energies of PFOSF and resultant PFOS from photocatalytic substitution reaction of fluorine with hydroxyl radicals were determined using Gauss View software (Wallingford, CT, USA). Natural bond orbital (NBO) calculation was performed at the B3LYP/6-31G<sup>+</sup>(d) level.

#### 2.3.3. Mass spectrometric imaging of plant leaves

For mass spectrometric imaging analysis of PFOSF, plant leaves of *Cayratia japonica* were tightly pressed onto the top of the thin film of bismuth cobalt zinc oxide under 0.1 MPa pressure against the film. Fabrication of bismuth cobalt zinc oxide thin film has been described in our previous work [13–15]. Glue tapes were attached to short stems in order to fix the position of the leaves on the film. Stock solution of PFOSF in methanol was deposited as a letter of “F” on the surface of leaf. Waters MALDI Imaging Pattern Creator (Billerica, MA, USA) software was used to define the imaging areas before subject to laser shotting. The step size of laser beams scanning across the leaves was set as 80  $\mu$ m  $\times$  80  $\mu$ m. Decreased step size improves spatial resolution but it takes longer time to establish the imaging. For each pixel, the acquisition time is 1 s.

## 3. Results and discussion

### 3.1. Photocatalytic substitution of fluorine of PFOSF with hydroxyl radicals on different substrates

Experimental evidences have revealed that transformation of PFOSF to PFOS is very slow even at temperature more than 150 °C. It has long been thought that PFOSF is very stable and not subject to photolysis [16]. Then we are very interested in the experimental fact that photocatalytic substitution of fluorine atom of PFOSF reproducibly occurs on surfaces of semiconductor nanoparticles and metal substrates. Fig. 1(A–C) show the MS spectra in negative ion mode of PFOSF that was deposited on surfaces of  $(\text{Bi}_2\text{O}_3)_{0.07}(\text{CoO})_{0.03}(\text{ZnO})_{0.9}$  (A),  $\text{TiO}_2$  (B) and BN (C) nanoparticles respectively. The bias voltage between the sample plate and the aperture is 20 V. Instead of the molecular ion at  $m/z$  501.9332 Da, ions at  $m/z$  498.9297  $\pm$  0.0009 Da with different intensities were observed on all three semiconductors. The 3.0035 Da mass differences are exactly the same as that between the fluorine atom (18.9984 Da) and oxygen atom (15.9949 Da). The experimental result suggests

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