Directional Electron Transfer Mechanisms with Graphene Quantum Dots as the Electron Donor for Photodecomposition of Perfluorooctane Sulfonate

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ABSTRACT

Graphene quantum dots (GQDs) were synthesized via the oxygen-driven unzipping of graphene under ultra-high frequency ultrasonication, and then attached to the SiC nanoparticles by the hydrothermal method to form the SiC/GQDs nanocomposites. The SiC/GQDs exhibited superior photoactivity over the decomposition of perfluorooctane sulfonate ($\text{C}_8\text{F}_{17}\text{SO}_3\text{H}$, PFOS), which was even harder to decompose than perfluorooctanoic acid (PFOA). This work presented the first instance of employing photoexcited semiconductor nanomaterials to realize the improvement from the activation of the $-\text{F}_2\text{C}-\text{COOH}$ bond in PFOA to the activation of $-\text{F}_2\text{C}-\text{SO}_3\text{H}$ in PFOS. The decomposition rate constants (k) of 2- CF_3 -PFOS, 6- CF_3 -PFOS and linear-PFOS with SiC/GQDs were 0.127 h^{-1} , 0.115 h^{-1} , 0.098 h^{-1} , and the corresponding half-lives were 5.5 h, 6.0 h, 7.1 h, respectively. The ratio of k (the branched isomers : the linear isomers) significantly reduced from the 967 times via vacuum ultraviolet (VUV) photolysis to the same order of magnitude in this work. The X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were conducted to investigate the electronic properties of SiC/GQDs, revealing the centermost directional electron transfer process during the reaction. The photogenerated electron originated from the $\pi-\pi^*$ transition of the $\text{C}=\text{C}$ bond and the $\text{n}-\pi^*$ transition of the $\text{C}=\text{O}$ bond under UV excitation, transferred to SiC nanoparticles due to the heterojunction structure of SiC/GQDs, and then further transferred to the accumulated PFOS on the surface of SiC/GQDs for the electron-withdrawing property of sulfonate group, leading to the critical activation of sulfonate group. The decomposition mechanisms of PFOS involved the ionic headgroup cleavage, hydrolysis, hydrodefluorination, and the C-C bond scission.

Keywords: Perfluorooctane Sulfonate (PFOS); Graphene quantum dots; Heterojunction; Electron transfer; Sulfonate activation; Hydrodefluorination

1. Introduction

Perfluorooctane sulfonate ($C_nF_{2n+1}SO_3H$, PFOS) has been regulated to limit future manufacturing by the United States Environmental Protection Agency (USEPA), while a limited set of existing uses (metal finishing, plating baths, and semiconductor etching) is excluded from the regulations because these uses are ongoing and alternative are not available [1]. The widespread uses have resulted in the global occurrence of PFOS and related derivatives either from direct use of PFOS, as well as from indirect sources like degradation of perfluorooctane sulfonate precursors (PreFOS) [2, 3]. The concentration of PFOS ranges from several to dozens of $ng\ L^{-1}$ levels in natural waters, and the concentration can be as high as $120\ \mu g\ L^{-1}$ (ground water) and $2210\ \mu g\ L^{-1}$ (surface water) in airports or other polluted areas [4-6]. PFOS has developmental toxicity, immunotoxicity, and hepatotoxicity and can be bio-accumulated in the human body and wildlife tissues, posing potential health risks [7, 8]. PFOS was thus added as the persistent organic pollutants (POPs) to Annex B of the Stockholm Convention in 2009 [9]. To address the impending risks posed to the environment, the efficient and economical technologies for PFOS disposal have become a practical need particularly in the frame of global implementation of the Stockholm Convention.

Persistence of perfluoroalkyl compounds (PFCs) is mainly caused by their intrinsic bond strengths ($C-F$, $531.5\ kJ\ mol^{-1}$) [10]. Compared with perfluorooctanoic acid (PFOA), PFOS is even more difficult to degrade for the presence of strong electron-withdrawing headgroup — sulfonate group [11, 12]. PFOS is inert to many methods that can efficiently decompose PFOA, such as electrochemical oxidation with $Ti/SnO_2-Sb/PbO_2$ anode, photocatalysis with commercial nano- TiO_2 (Degussa P25), and photolysis under UVC light. According to the previous researches, PFOS decomposition started with the cleavage of $-F_2C-SO_3H$ bond, thus the focus of PFOS decomposition was how to realize initial activation of sulfonate group [13, 14]. Sulfonate group in PFOS is

recalcitrant to traditional advanced oxidation processes (AOPs), while the hydrated electron (e_{aq}^-) induced reduction has been recently demonstrated to be effective to activate the sulfonate group [15, 16]. However, due to the high reactivity of e_{aq}^- with other coexistent oxidative species in solution, a large amount of chemical agent (molar concentration, $I^- : PFOS = 500 : 1$) that can promote the e_{aq}^- production was necessary to ensure fast decomposition kinetics [16]. Inspired by these researches, conduction band electron (e_{cb}^-) generated by light irradiation with strong reduction ability as well, can probably substitute for e_{aq}^- to activate the sulfonate group. Moreover, different from the free diffusion of e_{aq}^- during the reaction, photogenerated e_{cb}^- can directionally transfer to the electron acceptor — PFOS, which is accumulated on the surface of hydrophobic nanomaterials as the surfactant. This process provides the possibility to activate sulfonate group via directional electron transfer, reducing the transfer distance of electron and minimizing the competitive reaction to further increase the proportion of electron participates in the reaction and optimize the decomposition of PFOS.

To the best of our knowledge, there is still no report on the PFOS decomposition with photoactivated semiconductor nanomaterials, that can realize the cleavage of $-F_2C-SO_3H$ bond via the sulfonate activation under UV excitation. In our previous work, it was demonstrated that photoinduced generation of the Si-H bond on the metal-free SiC nanoparticle can efficiently decompose perfluorooctanoic acid (PFOA) via the Si-H/C-F redistribution (conversion into Si-F/C-H) [17]. Considering the analogous molecule structures of perfluoroalkyl radical ($C_nF_{2n+1}^\bullet$) after the headgroup cleavages of PFOA and PFOS, new questions are thus proposed based on the that work: can SiC provide sufficient photogenerated electron to activate the sulfonate group in PFOS, can the $C_nF_{2n+1}^\bullet$ in PFOS react with SiC in the similar way to realize the subsequent PFOS decomposition, and will the decomposition efficiency be further improved by introducing other

co-catalysts?

Quantum dots (e.g., CdS, CdSe, PbS), as the typical zero-dimensional nanomaterial, possess high reactivity for the large ratio of surface atoms and have been well demonstrated to effectively improve the photoelectrical and photochemical properties of semiconductor materials as the co-catalyst [18-20]. However, their large-scale applications are heavily impeded by the potential environmental hazard for the release of heavy-metal ions. Graphene quantum dots (GQDs) have attracted considerable attention nowadays for the excellent properties, such as low toxicity, low cost, chemical inertia, and biocompatibility [21, 22]. It is still unknown whether GQDs can work as the suitable co-catalyst to promote the decomposition of PFOS.

The objective of this work was to investigate the decomposition mechanisms of PFOS under UV light irradiation with as-synthesized SiC/GQDs nanocomposites. The decomposition kinetics of branched and linear PFOS isomers under different conditions (with SiC/GQDs, with SiC, direct photolysis) was investigated. The transformation of PFOS was inferred based on the qualitative and quantitative analyses of intermediates, and the mass balance of fluorine and sulfur elements. The mechanisms responsible for PFOS decomposition were further discussed by elaborating the electron transfer process, with the aid of optical properties and electronic structure analyses of SiC/GQDs.

2. Materials and methods

2.1. Reagents and Materials

Silicon carbide (SiC, 99.9%) was obtained from Sigma-Aldrich Chemicals in Saint Louis, USA. Potassium perfluorooctane sulfonate ($C_8F_{17}SO_3K$, 98%) was purchased from Matrix Scientific in Columbia, USA. Graphene nanoplatelets (Graphene, 99.9%) were purchased from Strem Chemicals in Newburyport, USA. Potassium iodide (KI, 99%), isopropyl, ethanol, acetic acid, concentrated sulfuric acid, concentrated nitric acid and ammonia solution were supplied by Sinopharm in Beijing,

CHN. All chemicals used in the experiments were the analytical grade or higher, and were used as received without further purification. Solutions were prepared with ultrapure/deionized water throughout the experiments by Milli-Q purification system.

2.2. *Synthesis of GQDs and SiC/GQDs*

One hundred mg graphene was dispersed in concentrated nitric acid (60 mL) and sulfuric acid (20 mL), fully oxidized and unzipped by ultra-high frequency ultrasonication (800 kHz, 350 W) for 30 h. Then the mixture was diluted with deionized water (200 mL) and centrifuged to remove any impurities. The purified mixture was re-dispersed in deionized water (40 mL) and ammonia solution (5 mL, 13.80 mol L⁻¹), and then sealed in Teflon container at 110 °C for 4 h. Finally, the resulting light yellow solution was further dialyzed by dialysis bag (retained molecular weight: 3500 Da). The concentration of GQDs solution was determined to be ~80 mg L⁻¹ by total organic carbon (TOC) analysis.

Five hundred mg of SiC was dispersed in 6.25 mL GQDs solution and 23.75 mL deionized water. After ultrasonication for 50 min, the mixture was transferred into Teflon container at 140 °C for 5 h. Then the samples were separated by centrifugation and washed five times with ethanol and deionized water to remove any impurities. The SiC/GQDs nanocomposites were finally vacuum freeze dried at -60 °C and stored for the following experiments.

2.3. *Characterization*

Photoluminescence (PL) spectrum was carried out on a spectrometer (TemPro-01, Horiba Jobin Yvon; Paris, FRA), the excitation wavelength and the corresponding emission wavelength were 250-370 nm and 360-480 nm, respectively. UV-vis absorption spectrum was recorded on a spectrophotometer (DR 6000, Hach; Loveland, USA) in the wavelength range from 200 nm to 500 nm.

X-ray photoelectron spectroscopy (XPS) spectra data was measured by an XPS system (ESCALAB 250Xi, ThermoFisher; Waltham, USA) with the monochromatic Al K α radiation (1486.6 eV). Survey analysis in the whole range of X-ray spectra and high-resolution analyses in the typical zone of C-1s, O-1s, Si-2p were performed. Ultraviolet photoelectron spectroscopy (UPS) was conducted using a UPS system (ESCALAB 250Xi, ThermoFisher; Waltham, USA) with the He(I) resonance 584 Å radiation of 21.217 eV for the valence band (VB) energy region measurements.

The SiC/GQDs nanocomposites were characterized by high-resolution transmission electron microscopy (HRTEM) to investigate the physical structures, detecting the lattice parameter of SiC/GQDs. HRTEM images were obtained by a transmission electron microscope (Tecnai TF-20, Philips; Eindhoven, NED) operated at an accelerating voltage of 200 kV. Samples for HRTEM images were prepared by dispersing the SiC/GQDs ethanol solution on ultra-thin holey carbon film and dried at room temperature (25 ± 1 °C). X-ray powder diffraction (XRD) was conducted to investigate the phase structures. XRD measurement was performed on an X'Pert Pro MPD (PANalytical; Almelo, NED) with Cu K α radiation ($\lambda = 1.5418$ Å), and the scan rate was 5° min^{-1} within the 2θ range (20° to 80°). Total organic carbon (TOC) concentration of GQDs was analyzed by TOC machine (TOC-LCPH, SHIMADZU; Kyoto, JPN) according to the 680 °C combustion catalytic oxidation method.

2.4. Decomposition Procedures

The heterogeneous decomposition of PFOS was conducted in a cylindrical reactor (volume, 80 mL; diameter, 50 mm; height, 120 mm) equipped with a 254 nm UV lamp (5 W, Cnlight; Guangdong, CHN) as irradiation source in all laboratory batch experiments. UV lamp was placed inside the reactor with a quartz tube as waterproof (diameter, 26 mm; height, 110 mm), and the thickness of solution was 12 mm, reducing the loss of light energy during the photon transfer process.

The concentration of PFOS solution was $0.019 \text{ mmol L}^{-1}$ throughout the whole work. The solution was stirred for 0.5 h in darkness to ensure the establishment of an adsorption-desorption equilibrium of the suspension composed of PFOS solution and 40 mg SiC/GQDs nanocomposites. The decomposition experiment was performed under stirring at the speed of 800 r min^{-1} , ensuring the well dispersion of SiC/GQDs. Preliminary experiments indicated that there was no further adsorption of PFOS on SiC/GQDs after 0.5 h. The experiments were carried out for 20 h duration to evaluate the activity of SiC/GQDs nanocomposites for PFOS decomposition. In order to avoid the evaporation of aqueous solution caused by long-term illumination, the parafilm was used to seal the reaction system. Samples were collected at intervals for triple-stage quadrupole mass spectrometry (TQ-MS/MS) analyses: typically, at 0 h (the dynamic adsorption-desorption equilibrium), 4 h, 8 h, 12 h, 16 h and 20 h. The sampling volume was 0.5 mL, and the total sampling volume was 3 mL, 3.75% of the initial volume. Taking samples thus slightly affected the concentration of PFOS. Each sample was filtered through a polycarbonate membrane ($0.45 \text{ }\mu\text{m}$) to separate SiC/GQDs powder from the suspension. The control experiments suggested that the adsorption by ultrafilter was negligible, nor the evaporation during the decomposition process.

The concentration of PFOS and identification of intermediate products were analyzed by a TQ-MS/MS (API 3200, Applied Biosystems; Foster, USA) operating in negative electrospray mode. Multiple reaction monitoring (MRM) experiments were performed with a gradient mobile phase which was composed of solvent A (methanol) and solvent B (5 mmol L^{-1} ammonium acetate): 0 – 5.0 min, methanol gradient increased from 70% to 95%; 5.0 – 8.0 min, held solvent A at 95%; 8.0 – 8.1 min, linear decrease of solvent A from 95% to 70%; 8.1 – 13.0 min, held this proportion.

The concentrations of fluoride ion (F^-), sulfonate ion (SO_4^{2-}) in aqueous solution were determined by an ion-chromatograph system (ICS-1100, Dionex; Sunnyvale, USA). The system was

equipped with the separation column (Dionex IonPac AS 12A, 4 mm $\times$ 200 mm) operating at 30 °C. The mobile phase was 20 mmol L⁻¹ KOH, and the flow rate was set at 1.0 mL min⁻¹.

3. Results and discussion

3.1. PFOS Decomposition Kinetics

The results of PFOS decomposition under various conditions are exhibited in Figure 1. The ¹⁹F nuclear magnetic resonance (NMR) spectra results of technical-PFOS by (CF₂ region) are shown in Figure S1, containing linear-PFOS, 2-CF₃-PFOS, and 6-CF₃-PFOS isomers. Neither direct photolysis nor addition of SiC under 254 nm UV irradiation decomposed technical-PFOS. While the SiC/GQDs efficiently decomposed both the branched and linear isomers, and the decomposition process well followed the pseudo-first-order reaction kinetics. The decomposition rate constants (k) for 2-CF₃-PFOS, 6-CF₃-PFOS and linear-PFOS were 0.127 h⁻¹ ($R^2 = 0.98$), 0.115 h⁻¹ ($R^2 = 0.99$), 0.098 h⁻¹ ($R^2 = 0.99$), and the corresponding half-life periods were 5.5 h, 6.0 h, 7.1 h, respectively. What deserved attention, decomposition rates for the branched isomers and the linear isomer were of the same order of magnitude. In the published papers, however, the branched isomers decomposed much more quickly than the linear isomer (direct VUV photolysis, the degradation rate of branched isomers is 967 times as fast as that of linear isomers; vitamin B₁₂ reduction, only applicable for the branched isomers and inert to the linear isomers) [23, 24]. This significant difference in experimental phenomenon should be attributed to the different decomposition mechanisms that would be discussed in detail later. After all, the SiC/GQDs was proved to be effective for decomposition of technical-PFOS.

Figure 1 and Table 1 here

3.2. Intermediate Analyses of PFOS

MRM results of intermediates are exhibited in Figure 2, that was detected by TQ-MS/MS to explore the PFOS decomposition process. A series of short-chain perfluorocarboxylic acids (PFCAs) including $\text{C}_3\text{F}_7\text{COO}^-$ (PFBA), $\text{C}_4\text{F}_9\text{COO}^-$ (PFPeA), $\text{C}_5\text{F}_{11}\text{COO}^-$ (PFHxA), $\text{C}_6\text{F}_{13}\text{COO}^-$ (PFHpA) and $\text{C}_7\text{F}_{15}\text{COO}^-$ (PFOA), were detected during the decomposition process at 1.99, 2.36, 2.95, 3.76, 4.64 min, respectively. None of short-chain PFCAs was detected at the beginning of the reaction (0 h), and the concentrations of those intermediates were time-dependent during the reaction. With the increase of reaction time, the concentrations of PFOA, PFHpA and PFHxA increased to the peak ($0.25 \mu\text{mol L}^{-1}$, $0.32 \mu\text{mol L}^{-1}$ and $0.80 \mu\text{mol L}^{-1}$, respectively) at 16 h, and the concentrations of PFPeA and PFBA increased continuously ($0.67 \mu\text{mol L}^{-1}$ and $1.23 \mu\text{mol L}^{-1}$ after 20 h, respectively) throughout the whole decomposition process. These observations demonstrated that short-chain PFCAs was probably formed through a stepwise C-C bond scission during the PFOS decomposition.

Figure 2 here

3.3. Mass Balance of Sulfur and Fluorine Elements

To further analyze PFOS decomposition process, the mass balance of sulfur and fluorine elements were investigated in this work. The concentrations of F^- and SO_4^{2-} in the solution were zeroed at 0 h to avoid the influence of original impurity in technical-PFOS. The contents of three main isomers in technical-PFOS from Matrix Scientific were as follows: linear-PFOS, 62.3% ; 2-CF₃-PFOS ,22.0% ;6-CF₃-PFOS ,11.4% [25]. The mass balance of sulfur was $78.8\% \pm 6.6$ for the SO_4^{2-} in solution, and $10.1\% \pm 3.4$ for the sulfonate group in undecomposed PFOS. The mass

balance of fluorine was $22.6\% \pm 4.0$, $9.3\% \pm 4.2$ and $10.1\% \pm 3.4$ for the F^- in solution, the fluorine in short-chain PFCAs and undecomposed PFOS, respectively. The mass balance of sulfur exhibited a high recovery rate (up to $\sim 88.9\%$). As for fluorine element, it was obviously that there was $\sim 58.0\%$ fluorine element unrecovered. The control experiment was performed by addition of HF solution into the reactor, and there was no notable decrease of F^- concentration after 7 days, suggesting F^- hardly adsorbed to the inner wall of the reactor. Where was the rest fluorine element? To answer this question, we conducted the XPS analyses of SiC/GQDs (collected before and after the decomposition), as shown in Figure S2. There was significant fluorination on the surface of SiC/GQDs, it was similar to the result we reported in the PFOA decomposition. The F^- detected in solution can be thus ascribed to the hydrolysis process of intermediates, and the unrecovered fluorine element probably mainly composed of the Si-F bond that generated during the hydrodefluorination of short-chain PFCAs [17].

Figure 3 here

Based on the analyses of intermediates and mass balance, we can demonstrate that decomposition of PFOS included hydrolysis and hydrodefluorination, which we have already well proved in the previous work. Then why SiC was not feasible in this reaction system and how the introduce of GQDs changed the decomposition process, that still needs the further experiment.

3.4. The Optical and Electronic Properties of SiC/GQDs

To elucidate the effect of GQDs in the reaction, it was of vital importance to investigate the physical, optical and electronic properties of the prepared GQDs. Characterization of the as-synthesized SiC/GQDs nanocomposites by high-resolution transmission electron microscopy

(HRTEM) showed the highly uniform dispersion of GQDs (1.8 to 3.6 nm in diameter) embedded onto the SiC nanoparticles (Figure S3). UV-vis absorption and fluorescence emission-excitation spectrum are shown in Figure 4. GQDs presented two typical absorption peaks at 310 nm and 340 nm from Figure 4a, which corresponded to the intrinsic peaks (Peak A and Peak C) of the PL excitation (PLE) in fluorescence emission-excitation map. As shown in Figure 4a, the absorption peak at 310 nm can be assigned to the π - π^* transition of aromatic sp^2 -hybridized domains (π^* stands for the antibonding orbital of π orbital), and the peak at 340 nm can be attributed to the n - π^* transition of the surface oxygen defect (n stands for the oxygen nonbonding orbital) [26, 27]. Moreover, with the excitation wavelength increased from 250 nm to 370 nm, the relative PL peak shifted to longer wavelengths in the range of 360 nm to 480 nm. The GQDs exhibited the excitation-wavelength-dependent PL behavior, which was caused by the presence of defect states (composed of oxygen-containing functional groups) [28]. According to the above analyses, we can demonstrate the n orbital in HOMOs of GQDs, which was probably generated by the oxygen-driven unzipping of graphene.

As shown in figure 4b, two electronic transitions of 260 nm (4.77 eV, Peak A) and 310 nm (4.00 eV, Peak B) were observed in PLE spectrum, those can be regarded as the transitions of electrons from the σ and π orbitals (in highest occupied molecular orbitals, HOMOs) to the lowest unoccupied molecular orbitals (LUMOs) [29]. This phenomenon probably originated from zigzag edges of the GQDs periphery, related to the carbene-like triplet ground-state multiplicity ($\sigma^1\pi^1, \sigma^2$) [30]. The calculated energy difference (δE) of GQDs between the σ and π orbitals was 0.77 eV. In previous research, methylene was taken as the example to estimate the δE between these two orbitals, the maximum δE for a triplet ground state should be no more than 1.5 eV [31]. That was in accordance with our results, suggesting the assignment of these two transitions was reasonable.

From these optical properties analyses of GQDs, we can demonstrate the possible transitions of photogenerated electron in GQDs from the σ , π and n orbitals in HOMOs to LUMOs under 254 nm UV excitation.

Figure 4 here

High-resolution XPS spectrum was performed to analyze the electronic structure of SiC/GQDs. The typical C-1s spectrum (Figure 5a) exhibited four distinct peaks located at 282.8 eV, 284.8 eV, 286.0 eV and 288.8 eV, corresponding to the Si-C, C=C (aromatic sp^2 -hybridized carbon), C-O (hydroxyl groups) and C=O (carbonyl groups) bond, respectively [32, 33]. The O-1s spectrum (see Figure S4 of the SI) can be resolved into two components at 531.2 eV and 533.5 eV, which were associated with the C-O and C=O bonds, respectively [34]. Those specific oxygen-containing functional groups on the surfaces can make GQDs stable to attach to the SiC nanoparticle surfaces [35]. The two absorption peaks observed in Figure 5 can be attributed to the transitions of C=C and C=O bonds [36]. However, compared with the previous work, the peak at ~290.1 eV, which corresponded to C=O-OH groups was not observed, the probable reason was that these carboxyl groups were efficiently reduced by ammonia in the hydrothermal process [34]. According to the XPS results, it can be further inferred that the transitions of photogenerated electron inside GQDs were mainly attributed to the π - π^* transition of the C=C bond and the n - π^* transition of the C=O bond.

Aside from the efficient electron transitions of GQDs, the proper conduction band level of SiC/GQDs is also important to offer strong reductive e_{cb}^- to lead to activation of sulfonate group. Ultraviolet photoelectron spectroscopy (UPS) was thus performed to determine the ionization

potential (equivalent to the valence band energy (E_v)) of SiC and SiC/GQDs nanocomposites [37]. The E_v of SiC/GQDs nanocomposites and *n*-type SiC were calculated to be -4.77 and -5.83 eV (vs. Vacuum) by subtracting the width of the He I UPS spectra (Figure 5b) from the excitation energy (21.22 eV). Considering the band gap (E_g) value (3.00 eV for both SiC and SiC/GQDs) determined from Figure S5, the conduction band energy (E_c) of SiC/GQDs nanocomposites and SiC were thus estimated to be -1.77 and -2.83 eV from $E_v - E_g$, respectively. The UPS results demonstrated that addition of GQDs significantly improved the E_c and E_v of SiC/GQDs compared with SiC. Based on the above results, we proposed that the quantum confinement effect led to a discrete energy level distributions of GQDs, and the formed HOMOs and LUMOs are higher than the corresponding E_v and E_c of SiC, respectively. The previous research performed density functional theory (DFT) to calculate the theoretical HOMO (-5.66 eV) and LUMO (-0.68 eV) of GQDs, which was in accordance with our experimental results [38]. The heterojunction structure can be thus formed in SiC/GQDs due to the energy level matching, and it can efficiently improve the photoactivity by suppressing the recombination of the photogenerated carriers.

Figure 5 here

The photogenerated electrons originated from the π - π^* transition of the C=C bond and the n - π^* transition of the C=O bond, and then transferred from the LUMOs of GQDs to the conduction band (CB) of SiC nanoparticles, the photogenerated holes transferred from the valence band (VB) of SiC to the HOMOs of GQDs, improving the separation efficiency of the photogenerated carriers remarkably. What's more, a short electron pathway between the GQDs interior and the surface due to the quantum size can enhance the electron transfer as well [39]. GQDs acted as the electron

donors in this process, in which electrons can be easily transferred to the surface of SiC nanoparticles. And then PFOS, which accumulated on the surface of SiC due to the surface-active properties, would act as the final electron acceptor for the electron-withdrawing property of sulfonate group. This electron transfer process can lead to the ionic headgroup cleavage (the sulfonate group) from PFOS, forming the perfluoroalkyl radicals ($C_8F_{17}\bullet$). The initial directional electron transfer process was thus of great importance to the PFOS decomposition. SiC can hardly offer sufficient e_{cb}^- to activate the sulfonate group without GQDs as the electron donor, that was probably the reason why SiC/GQDs is feasible for PFOS decomposition instead of SiC.

3.5. Decomposition Mechanisms of PFOS

Based on the above experimental results, the mechanisms for the photochemical transformation of PFOS in the presence of SiC/GQDs under UV irradiation is proposed in Figure 6. The electron was generated by the UV excitation of SiC/GQDs, and then decomposition of initial PFOS started with the electron transfer process. As soon as PFOS gained the electrons, the electron-mediated reduction occurred at the chain-terminal sulfonate group. One of the original S=O bonds transformed into the S-O bond, forming one unpaired electron on the S atom and one O^- ion with the outer layer filled with eight electrons ($PFOS^{\bullet 2-}$). $PFOS^{\bullet 2-}$ inclined to react with H^+ , leading to the loss of OH^- and yielding $C_nF_{2n+1}SO_2\bullet$. $C_nF_{2n+1}SO_2\bullet$ subsequently dissociated into $C_nF_{2n+1}\bullet$ and SO_2 [11]. Since SO_2 was easily dissolved into the solution, and the reaction system was sealed with parafilm, most of the generated SO_2 transformed into SO_4^{2-} and was detected by the ion-chromatograph. As for $C_nF_{2n+1}\bullet$, it can react with H_2O to form the unstable $C_nF_{2n+1}OH$, then $C_nF_{2n+1}OH$ converted into $C_{n-1}F_{2n-1}COF$ by intramolecular rearrangement, and subsequently transformed into the short-chain PFCAs via hydrolysis [40]. In this way, F^- was generated during the hydrolysis process. While based on the low concentration of F^- detected in the solution, it was

obviously that this hydrolysis is not the main pathway for $C_nF_{2n+1}\bullet$ decomposition. On the other hand, the fluorine atoms at the chain-terminal of $C_nF_{2n+1}\bullet$ were gradually replaced by hydrogen atoms due to the nucleophilic substitution hydrodefluorination, the C-F bonds transformed into C-H bonds via the Si-H/C-F redistribution (conversion into C-H) [17]. The generated Si-F bonds were well demonstrated by the surface fluorination of SiC based on the XPS results. After all fluorine atoms at the chain-termination were replaced through the sequential F/H exchange, the CH_2 carbene was eliminated via the C-C scission due to the UV light excitation [17]. The generated short-chain PFCAs were detected by the TQ-MS/MS results for the qualitative and quantitative analysis, demonstrating this C-C scission. It is thus concluded that $C_nF_{2n+1}\bullet$ was decomposed via the hydrodefluorination and hydrolysis process, the hydrodefluorination should be the main pathway for $C_nF_{2n+1}\bullet$ decomposition.

Figure 6 here

According to previous research on VUV photolysis and UV/SO_3^{2-} , the branched PFOS decomposed much faster than the linear isomers [15, 22]. It was because that photon and e_{aq}^- directly reacted with PFOS molecule in solution, and the C-F bond in branched isomers was more vulnerable to reductive decomposition than the linear isomers for the higher electron affinity [41]. However, in our research, the photogenerated electron transited from the HOMOs to the LUMOs of GQDs, then influxed into the CB of SiC due to the matching energy levels between GQDs and SiC, and finally transferred to the accumulated PFOS on the surface of SiC/GQDs. The final step resulted from the strong withdrawing property of the sulfonate group instead of high electron affinity of the C-F bond, leading to the headgroup cleavage. Moreover, the F^- detected in solution was much less

than the F atom that bonded to the Si-terminations on SiC/GQDs, the main subsequent decomposition pathway of $C_nF_{2n+1}\bullet$ can be thus ascribed to the hydrodefluorination process. These different mechanisms mentioned above, compared with the previous researches, led to the experimental phenomenon that the branched isomers decomposed at the similar kinetics with linear isomers.

4. Conclusions

The PFOS decomposition is of increasing concern due to its global distribution. This work demonstrated both branched and linear PFOS can be effectively decomposed with SiC/GQDs under 254 nm UV irradiation. The photogenerated electrons originated from the π - π^* transition of the C=C bond and the n - π^* transition of the C=O bond, and then transferred from the LUMOs of GQDs to the conduction band (CB) of SiC nanoparticles due to heterojunction structure. PFOS transformed into $C_nF_{2n+1}\bullet$ via the directional electron transfer from SiC/GQDs due to the high electronegativity of fluorine atoms, and subsequently further decomposed to short-chain PFCAs by the hydrolysis and hydrodefluorination. Results in the present study have the inspirational significance for research on PFCs decomposition in the aqueous environment. Further work is necessary to determine the toxicity of the decomposition products and the inactivation kinetics in the presence of dissolved organic matter (DOM, e.g. humic acid, fulvic acid) and other coexistent ions (e.g., Cl^- , NO_3^- , SO_4^{2-} , CO_3^{2-}/HCO_3^-) to test the feasibility of this reaction system in natural or complex water matrix.

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Table 1 Decomposition kinetics and the electrical energy per order parameter (*EEO*) of technical-PFOS

No.	Technical-PFOS ^a	Decomposition ratios (%)	Decomposition rate constants (<i>k</i> , h ⁻¹)	Half-lives (h)	<i>R</i> ²	<i>EEO</i> ^b (kWh/m ³ /order)
1	linear-PFOS	88.5	0.098	7.1	0.98	1.47
2	2-CF ₃ -PFOS	93.9	0.127	5.5	0.99	1.13
3	6-CF ₃ -PFOS	90.4	0.115	6.0	0.99	1.25

^a The initial concentration of technical-PFOS is 0.019 mol L⁻¹.

^b The electrical energy per order parameter, defined as the number of kilowatt-hours (kWh) of electrical energy required to reduce the concentration of a pollutant by one order of magnitude (90%) in 1 m³ contaminated water, adopted by the International Union of Pure and Applied Chemistry (IUPAC).

Figure Captions

Figure 1. Pseudo-first-order kinetic plots of PFOS ($0.019 \text{ mmol L}^{-1}$) under 254 nm UV light irradiation in the presence of SiC/GQDs (0.5 g L^{-1}) at room temperature ($25 \pm 1 \text{ }^{\circ}\text{C}$), and the pH value was 7: (a) decomposition rates of 2-CF₃-PFOS isomers, (b) decomposition rates of 6-CF₃-PFOS isomers, (c) decomposition rates of Linear-PFOS isomers.

Figure 2. (a) Multiple reaction monitoring (MRM) results of PFOS detected by triple-stage quadrupole mass spectrometry (TQ-MS/MS) at room temperature ($25 \pm 1 \text{ }^{\circ}\text{C}$). These short-chain perfluorocarboxylic acids (PFCAs) including C₃F₇COO⁻ (PFBA), C₄F₉COO⁻ (PFPeA), C₅F₁₁COO⁻ (PFHxA), C₆F₁₃COO⁻ (PFHpA) and C₇F₁₅COO⁻ (PFOA) were detected during the decomposition process at 1.99, 2.36, 2.95, 3.76, 4.64 min, respectively; (b) the concentration variations of intermediates, as a function of decomposition time.

Figure 3. Mass balance of fluorine element and sulfur element during the decomposition process at room temperature ($25 \pm 1 \text{ }^{\circ}\text{C}$). The dosage of SiC/GQDs was 0.5 g L^{-1} , the wavelength of UV light was 254 nm, the pH value was 7, and the concentration of PFOS was $0.019 \text{ mmol L}^{-1}$.

Figure 4. Characterization of the optical properties of the graphene quantum dots (GQDs): (a) UV-vis absorption spectra of GQDs, (b) fluorescence emission-excitation map of the GQDs at different excitation wavelengths. GQDs were dispersed in water, and the experiments were performed at room temperature ($25 \pm 1 \text{ }^{\circ}\text{C}$).

Figure 5. Characterization of the electrical properties of the SiC/GQDs: (a) X-ray photoelectron spectroscopy (XPS) results of C-1s region high-resolution spectra of SiC/GQDs at room temperature ($25 \pm 1 \text{ }^{\circ}\text{C}$), (b) ultraviolet photoelectron spectroscopy (UPS) spectra of SiC and as-synthesized SiC/GQDs at room temperature ($25 \pm 1 \text{ }^{\circ}\text{C}$). The dashed black lines mark the baseline and the dashed red lines indicate the tangents of the curve. The valence

band energy (E_v) can be calculated from the intersections of the tangents with the baseline,
(c) typical transfer of electrons and holes in the SiC/GQDs heterojunction structure under UV light excitation.

Figure 6. Decomposition mechanisms of PFOS with SiC/graphene at room temperature (25 ± 1 °C).

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Graphical Abstract