



Directional electron transfer mechanisms with graphene quantum dots as the electron donor for photodecomposition of perfluorooctane sulfonate



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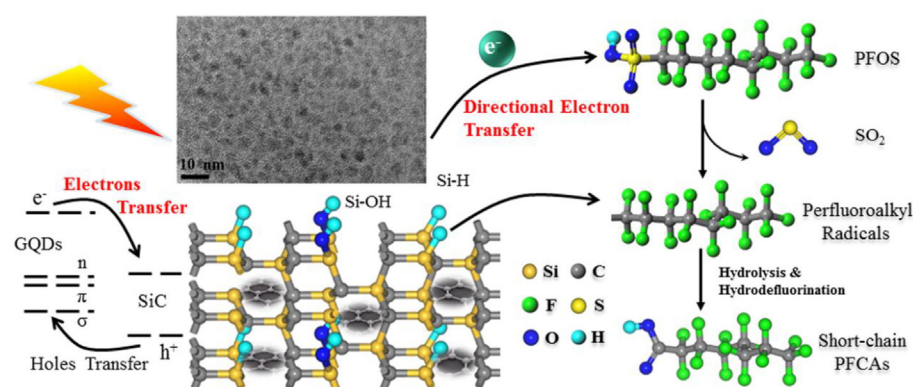
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HIGHLIGHTS

- Branched and linear PFOS isomers were efficiently decomposed with SiC/GQDs.
- GQDs formed the heterojunction with SiC and acted as the electron donor.
- Desulfonation of PFOS into $C_nF_{2n+1}^{\cdot}$ was caused by the electron transfer.
- $C_nF_{2n+1}^{\cdot}$ transformed into short-chain PFCAs mainly via hydrodefluorination.

GRAPHICAL ABSTRACT



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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 ($C_8F_{17}SO_3H$, 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 $-F_2C-COOH$ bond in PFOA to the activation of $-F_2C-SO_3H$ 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 center-most directional electron transfer process during the reaction. The photogenerated electron originated from the $\pi-\pi^*$ transition of the $C=C$ bond and the $n-\pi^*$ transition of the $C=O$ 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

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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. © 2017 Elsevier B.V. All rights reserved.

1. Introduction

Perfluorooctane sulfonate ($C_8F_{17}SO_3H$, 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 bioaccumulated 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 perfluoro-

roctanoic acid (PFOA) via the Si–H/C–F redistribution (conversion into Si–F/C–H) [17]. Considering the analogous molecule structures of perfluoroalkyl radical ($C_nF_{2n+1}\cdot$) 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 $C_nF_{2n+1}\cdot$ 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

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