

Photocatalytic Defluorination of Per- and Polyfluoroalkyl Substances: From Mechanistic Insights to Rational Design

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Abstract: Per- and polyfluoroalkyl substances (PFAS) pose severe threats to ecosystems and human health due to their extreme persistence, bioaccumulation, and toxicity. Their ultra-strong C–F bonds render them recalcitrant to conventional water treatment technologies, spurring growing interest in photocatalytic degradation as a promising alternative. This review establishes a photocatalytic PFAS treatment framework that focuses on defluorination. We systematically compare the contributions of various reactive species to PFAS defluorination and evaluate the primary degradation pathways based on their defluorination efficiencies and the toxicities of the resulting intermediates. Furthermore, key influencing factors and integrated design strategies are summarized to enhance defluorination performance. This review provides a roadmap for developing photocatalytic technologies capable of truly destroying per- and polyfluoroalkyl substances.

Keywords: Photocatalysis; PFAS; defluorination

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) have emerged as a global class of persistent organic pollutants due to their extensive presence in various environmental matrices, including surface water, groundwater, soil, and even biota worldwide [1–3]. As so-called “forever chemicals”, PFAS exhibit extraordinary persistence in the environment [4], which is primarily attributed to the exceptionally strong carbon-fluorine (C–F) bonds, with bond dissociation energies (BDEs) typically ranging from approximately 404 to 551 kJ mol^{−1} depending on the PFAS structure and the position of the C–F bond within the molecule [5]. For PFOA, for example, C–F BDEs of terminal –CF₃ groups are substantially higher (~493–518 kJ mol^{−1}) than those of internal –CF₂– units (~446–476 kJ mol^{−1}). These values rank among the strongest covalent bonds in organic chemistry. This inherent stability renders PFAS resistant to natural degradation processes such as hydrolysis, photolysis, and biodegradation, leading to their long-term accumulation in the ecosystem and subsequent bioaccumulation through the food chain [6]. Accumulating evidence has demonstrated that chronic exposure to PFAS poses significant adverse effects on human health, including but not limited to thyroid disorders, reproductive and developmental toxicity, immunotoxicity, and an increased risk of certain cancers [7,8]. Notably, the complete detoxification of PFAS cannot be achieved merely by shortening their carbon chains; instead, the cleavage of C–F bonds is recognized as the core



indicator for the ultimate harmlessness of PFAS. Therefore, the current core challenge in PFAS pollution control lies in achieving efficient and deep defluorination, rather than just the removal of PFAS molecules from environmental media.

The defluorination of PFAS faces substantial obstacles, mainly derived from the unique molecular structure of PFAS. The extremely high bond energy of C–F bonds makes them recalcitrant to cleavage by conventional oxidation-reduction systems, which are often ineffective in breaking these stable bonds under mild conditions [9]. Moreover, short-chain PFAS (with carbon chain length ≤ 6) exhibit even greater resistance to deep defluorination due to their specific structural characteristics, including smaller molecular size, stronger hydrophilicity, and more stable chemical configurations compared to long-chain PFAS [10]. To address PFAS pollution, various remediation technologies have been developed, including physical adsorption [11], electrochemistry [12], advanced oxidation processes [13], biodegradation [14], and thermal treatment. However, these technologies suffer from inherent limitations in terms of defluorination efficiency, defluorination completeness, and secondary pollution risks. For instance, physical adsorption merely transfers PFAS from the aqueous phase to the adsorbent without achieving degradation or defluorination, requiring subsequent disposal of the spent adsorbent and potentially causing secondary pollution. Traditional AOPs primarily focus on the oxidation of PFAS carbon chains but fail to effectively cleave C–F bonds, resulting in low defluorination efficiency and the formation of toxic intermediate products. Biodegradation of PFAS is extremely slow and inefficient due to their recalcitrance, making it impractical for large-scale application. In contrast, photocatalytic technology has attracted considerable attention as a promising approach for PFAS defluorination, owing to its ability to generate highly reactive species under mild conditions (e.g., room temperature and atmospheric pressure) that can potentially cleave C–F bonds [15]. Nevertheless, current photocatalytic defluorination technology still faces core challenges, including the lack of targeted active species for C–F bond cleavage, asynchrony between defluorination and carbon chain degradation, and significant interference from complex actual water environments, which severely restrict its practical application.

In recent years, several reviews have surveyed photocatalytic PFAS degradation from various perspectives, including the classification of heterogeneous photocatalysts [16], the mechanisms of photochemical degradation in homogeneous and heterogeneous systems [15], and the structure-function relationships in photocatalytic PFAS removal [17]. However, these reviews predominantly focus on degradation pathways or catalyst types, with limited systematic integration and evaluation centered specifically on defluorination efficiency—the critical metric that determines whether PFAS are truly destroyed rather than merely transformed. The present review differs conceptually from previous works in three aspects: (i) it establishes a defluorination-oriented framework that prioritizes fluoride release over parent compound degradation as the primary performance metric; (ii) it systematically compares the intrinsic capabilities of different reactive species for C–F bond cleavage and evaluates their respective defluorination efficiencies; and (iii) it synthesizes multi-dimensional design strategies—spanning electronic structure modulation, interface engineering, light absorption broadening, and macrostructural design—that are explicitly linked to enhancing defluorination performance. This framework aims to guide the rational development of photocatalytic systems capable of achieving deep defluorination rather than merely removing PFAS from water.

2. Mechanisms of Photocatalytic PFAS Defluorination

2.1. Active Species for PFAS Defluorination

In photocatalytic and photochemical systems, reactive species govern the selectivity and efficiency of C–F bond breaking and chain decomposition. To clarify the intrinsic structure–activity relationship between reactive species and defluorination performance, this section categorizes reactive species by their contribution to defluorination and elucidates their intrinsic capacity to cleave C–F bonds.

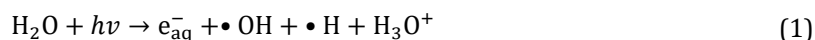
The reactivity of PFAS toward photogenerated species is determined by thermodynamic, kinetic, and physicochemical factors. While BDEs provide a fundamental measure of C–F bond strength, the accessibility of defluorination pathways is often dictated by activation barriers. For example, *ab initio* molecular dynamics simulations reveal that the activation barrier for C–F bond dissociation in PFOS upon electron injection is approximately three times larger than that in PFOA, rationalizing the higher recalcitrance of sulfonate-terminated PFAS [18]. Electron localization and solvation structure also critically influence electron attachment and bond cleavage by modulating the stability of transient intermediates [18]. Beyond these molecular-scale factors, collective behaviors—aggregation, micellization, and interfacial partitioning

driven by the amphiphobic nature of perfluoroalkyl chains—can substantially alter the local concentration and accessibility of PFAS to reactive species [19]. These interdependent factors collectively determine defluorination efficiency and must be considered in rational photocatalyst design.

2.1.1. Reductive Species

Reductive species are recognized as the core drivers for C–F bond cleavage in photocatalytic PFAS defluorination, among which hydrated electrons (e_{aq}^-), hydrogen radicals ($\bullet H$) and photogenerated electrons (e^-) play a dominant role, mainly through nucleophilic attack to induce heterolysis or homolysis of C–F bonds.

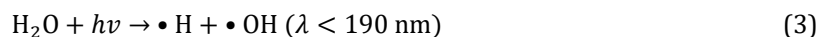
e_{aq}^- exhibit an ultra-negative redox potential (-2.9 V vs. NHE) that enables thermodynamically favorable electron attachment to the antibonding orbitals of C–F bonds, triggering heterolytic cleavage and rapid fluoride release without requiring preliminary activation of head groups [20]. e_{aq}^- can be generated through three primary pathways: (1) direct photolysis of water by high-energy photons ($\lambda < 200$ nm) (Equation (1)); (2) photoinduced electron transfer from donor molecules (e.g., SO_3^{2-} , I^-) to the aqueous phase (Equation (2)); and (3) injection of conduction band electrons from semiconductors into the aqueous phase. The UV/sulfite system, for example, produces e_{aq}^- via photolysis of SO_3^{2-} , achieving 98% PFOS degradation and 55% defluorination within 30 min [21], while the UV/iodide system delivers up to 98.8% PFOA defluorination [22]. More recently, photosensitizer-mediated systems such as UV/indole have been developed to improve e_{aq}^- yield and utilization by suppressing geminate recombination with $\bullet OH$, achieving $\sim 75\%$ defluorination under milder pH conditions [23]. Chen et al. further demonstrated a ternary indole/isopropyl alcohol (IPA) system in which IPA plays dual roles—scavenging oxygen and $\bullet OH$ to protect e_{aq}^- , and disrupting indole–PFOA hydrogen bonding at high indole concentrations—achieving $\sim 100\%$ PFOA degradation and 50.8% defluorination within 7 h, compared with $< 10\%$ degradation without IPA [24].



Despite these promising efficiencies, e_{aq}^- -based systems face inherent limitations. The generation of e_{aq}^- demands strictly anaerobic and highly alkaline conditions, and the species is severely quenched by dissolved oxygen (O_2 reacts with e_{aq}^- at near-diffusion-controlled rates, $k = 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) and protons. Park et al. [25] systematically characterized these constraints, demonstrating that competitive scavenging by triiodide (I_3^-) photoproducts substantially reduces the practical efficacy of the UV/iodide system—explaining the counterintuitive observation that PFOS degradation rates are lower in the UV/iodide system than in the UV/persulfate system despite the greater thermodynamic reducing power of e_{aq}^- . Moreover, the decay kinetics of perfluoroalkyl sulfonates depend strongly on perfluorocarbon chain length ($C_8 > C_6 > C_4$), whereas carboxylates exhibit minimal chain-length dependence. Extending this structure–reactivity analysis, Bentel et al. [26] examined 34 PFAS structures and identified the direct linkage between the fluoroalkyl chain and the carboxylate headgroup ($-COO^-$) as critical for rapid defluorination: perfluorocarboxylic acids exhibited consistently higher defluorination than fluorotelomer carboxylates or sulfonates of comparable chain length. Their work also delineated two competing pathways—H/F exchange (which stalls at partially hydrogenated intermediates) and the DHEH pathway (which enables stepwise CF_2 removal)—a mechanistic framework discussed in detail in Section 2.2.1.

$\bullet H$ have emerged as effective reducing species for PFAS defluorination (Equation (3)). In contrast to e_{aq}^- , for which PFAS-specific bimolecular rate constants have been reported for selected PFCAs and PFSAAs (e.g., $\sim 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for PFCAs [27] and chain-length-dependent values for PFSAAs [28]), PFAS-specific bimolecular rate constants for $\bullet H$ and activation barriers for $\bullet H$ -mediated C–F cleavage remain, to our knowledge, unavailable. Therefore, the rate constants currently available for $\bullet H$ —such as $\bullet H + O_2 \rightarrow \bullet HO_2$, $k = 2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and the $\bullet H + H_2O \rightleftharpoons e_{aq}^- + H_3O^+$ ($k = 2.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $pK_a = 9.6$), compiled by Buxton et al. [29]—are valuable benchmarks for $\bullet H$ generation, lifetime, and scavenging, but they do not directly quantify the reactivity of $\bullet H$ toward PFAS. Reduction potentials ($\bullet H$, -2.3 V vs. NHE at pH 7, e_{aq}^- , -2.9 V vs. NHE) provide thermodynamic context but are insufficient to predict PFAS reactivity, because $\bullet H$ can react via electron transfer, H-atom transfer, or addition, and the dominant pathway and its activation barrier are substrate-specific. Accordingly, we do not rank the intrinsic PFAS reactivity of $\bullet H$ and e_{aq}^- primarily on the basis of reduction potentials. The comparison is instead limited to system-level performance and operational constraints: e_{aq}^- -based systems can achieve very high defluorination under optimized conditions (e.g., 98.8% for PFOA in UV/iodide) but require strictly anaerobic and alkaline conditions and

are strongly quenched by O_2 and protons, whereas $\bullet H$ can be generated under ambient air and across broader pH ranges and is effective against diverse PFAS structures, although $\bullet H$ -driven defluorination alone often yields incomplete mineralization. Recent studies have elucidated distinct $\bullet H$ generation pathways. In conventional UV photolysis (254/365 nm), Qi et al. [30] demonstrated that $\bullet H$ arises from PFAS-derived perfluoroalkyl intermediates that activate water, rather than direct water photolysis. This mechanism operates across pH 3~11 and tolerates dissolved oxygen and most anions except nitrite. Vacuum UV (185 nm) generates $\bullet H$ via direct water homolysis [31], while ionizing radiation produces $\bullet H$ alongside e_{aq}^- and $\bullet OH$ [32]. These operational advantages make $\bullet H$ attractive for real water matrices, but they should not be interpreted as evidence for a higher intrinsic $\bullet H$ reactivity toward PFAS than that of e_{aq}^- ; resolving this question will require future measurements of PFAS-specific $k(\bullet H + PFAS)$ and ΔG values. Though $\bullet H$ -driven defluorination alone often yields incomplete mineralization, it can be generated without added chemicals and is effective against diverse PFAS structures, including ether-containing alternatives.



Photogenerated electrons (e^-) in heterogeneous photocatalysis enable sustainable reductive defluorination without continuous chemical dosing. Electron-enriched nanostructures—such as quantum dots and single-atom-modified semiconductors—significantly enhance this process. For example, CdS nanocrystals drive complete defluorination of PFOS under 405 nm visible-light irradiation via Auger recombination-induced hot electron injection, with catalyst reusability maintained over 12 cycles [33]. Similarly, in ZnS-[N] adsorptive photocatalysts, surface amine groups and lattice defects concentrate photogenerated electrons near adsorbed PFAS molecules, achieving over 90% defluorination of PFOA within 3 h [34]. Pt single-atom modified TiO_2 further improves electron utilization by trapping photogenerated e^- to form surface-active sites, promoting hydrodefluorination through hydrogen spillover effects [35]. Recent advances have extended this strategy to low-toxicity semiconductor nanocrystals, where multiphoton-driven processes—governed by the interplay of electronic structure, photophysics, and surface chemistry—enable efficient PFAS defluorination under mild LED irradiation [36]. Kanao et al. [37] demonstrated that acetate-capped ZnO nanocrystals achieve up to 92% defluorination of PFOS after 24 h of 365 nm LED irradiation under ambient conditions with high repeatability, whereas mercaptopropionic acid-capped ZnO nanocrystals achieved only 8.4% under identical conditions—underscoring that surface ligand engineering is decisive for PFAS adsorption and subsequent reduction.

Beyond inorganic photocatalysts, excited-state organic radical species have recently emerged as potent photoreductants for reductive defluorination. Upon photoexcitation, these molecular systems generate highly reducing excited states that inject electrons into fluorinated substrates via single-electron transfer (SET). Representative examples include the twisted carbazole-cored super-photoreductant KQGZ [38] (excited-state oxidation potential: -3.01 V vs. SCE , saturated calomel electrode; $E_{NHE} = E_{SCE} + 0.241$ at 25°C), neutral acridine radicals Mes-Acr $\bullet$ [39] (-3.36 V vs. SCE) capable of reducing inert aryl fluorides and chlorides, and the closed-shell species BPI-RO- H_2^{2-} [40] (generated from BPI/ nBu_4NF under blue light; -3.64 V vs. SCE) which enables direct C-F bond cleavage in organofluorines, PFAS, and fluorinated polymers. (detailed in Section 4.1.4)

Despite their high intrinsic defluorination capabilities, all reductive species are extremely susceptible to quenching by common aquatic matrix constituents, which severely constrains practical performance. Dissolved oxygen is the most critical scavenger: e_{aq}^- rapidly reacts with O_2 to form $\bullet O_2^-$, reducing defluorination efficiency from 88.5% under nitrogen to only 6.4% in aerated solutions [41]. This sensitivity, along with the alkaline pH requirements for e_{aq}^- generation and the incomplete mineralization of $\bullet H$ -driven processes, underscores the need for system-level design strategies (discussed in Section 4) to overcome these environmental barriers.

2.1.2. Oxidative Species

In contrast to reductive species, oxidative species including photogenerated holes (h^+), sulfate radicals ($SO_4^{\bullet-}$), singlet oxygen ($^1O_2$), and hydroxyl radicals ($\bullet OH$) generally do not directly cleave C-F bonds under mild photocatalytic conditions [42,43]. The perfluoroalkyl chain possesses an extremely low HOMO and lacks accessible electron-rich sites, so electron removal by these species is highly unfavorable; direct electron-transfer-driven C-F scission is therefore energetically demanding and kinetically unfavorable. C-F bond dissociation energies describe homolytic cleavage and are not equivalent to the electron-transfer thermodynamics that govern reactions with oxidative species. Consequently, these species act mainly as

auxiliary promoters by selectively oxidizing carboxylate or sulfonate head groups, thereby destabilizing PFAS molecules and creating favorable conditions for subsequent C–F cleavage.

Photogenerated h^+ represent the primary oxidative driver in heterogeneous photocatalysis, especially for semiconductors with highly positive valence band positions. Strong oxidative holes initiate direct electron abstraction from carboxylate groups, triggering Kolbe decarboxylation to form perfluoroalkyl radicals, which subsequently undergo stepwise chain shortening via hydroxylation, HF elimination, and hydrolysis. BiOCl, with a valence band potential of 3.60 V vs. NHE, enables highly efficient hole-mediated PFOA degradation, achieving 63% defluorination within 30 min under simulated sunlight [44]. Similarly, In_2O_3 forms bidentate complexes with PFOA, facilitating direct hole oxidation and achieving complete PFOA decomposition within 30 min under UV irradiation [45]. The novel photocatalyst $\text{Bi}_3\text{O}(\text{OH})(\text{PO}_4)_2$ (BOHP) exhibits 15-fold higher PFOA degradation kinetics than $\beta\text{-Ga}_2\text{O}_3$ due to favorable surface charge and strong hole oxidation capacity [46]. Complementing these heterogeneous systems, homogeneous photocatalysis using the water-soluble tungstic heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was demonstrated to achieve complete PFOA disappearance within 24 h under UV-visible irradiation, with an 88% fluoride yield and a turnover number of 4.33 at a 10:1 PFOA/catalyst molar ratio [47]. This system effectively suppressed the accumulation of short-chain perfluorocarboxylic acid intermediates and produced no CF_4 or other high-global-warming-potential byproducts, with reoxidation of the reduced polyoxometalate species by O_2 identified as the critical step for catalytic turnover.

$\text{SO}_4^{\bullet-}$ in homogeneous systems act as selective oxidative activators with high reactivity toward PFAS. Generated by UV photolysis of persulfate (Equation (4)), $\text{SO}_4^{\bullet-}$ ($E^\circ = 2.6\text{--}3.1$ V vs. NHE) selectively extracts electrons from carboxylate groups, achieving 100% PFOA degradation and 73.8% defluorination within 12 h [48]. The initial PFOA decomposition rate in this system was 11 times higher than that of direct photolysis, and all sulfur species were ultimately transformed to sulfate (SO_4^{2-}), simplifying waste stream management. A key insight from oxidative defluorination studies is the pronounced chain-length dependence: while PFCAs bearing $\text{C}_4\text{--}\text{C}_6$ perfluoroalkyl groups achieve complete parent compound decay, defluorination efficiencies decrease markedly with shorter chain length, reflecting the increasing recalcitrance of short-chain PFCAs toward oxidative attack. However, $\text{SO}_4^{\bullet-}$ -based oxidation suffers from significant limitations when applied to emerging PFAS structures. The sulfate radical is highly sensitive to steric hindrance: only 5% of GenX (HFPO-DA) is degraded after 3 h due to steric protection of the α -carbon by $-\text{CF}_3$ substituents [49]. Carbonate radicals ($\text{CO}_3^{\bullet-}$) [50] and nitrate radicals ($\text{NO}_2^{\bullet}$) [51,52] have also been reported to degrade PFOA through similar electron abstraction mechanisms, though their practical efficacy varies substantially depending on the water matrix. Thi et al. reported that in a $\text{UV}/\text{H}_2\text{O}_2/\text{NaHCO}_3$ system, $\text{CO}_3^{\bullet-}$ increased PFOA degradation from 32.3% to nearly 100% within 12 h. Yuan et al. found that the synergy of $\text{NO}_2^{\bullet}$ and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycle in a $\text{UV}/\text{Fe}(\text{NO}_3)_3$ system achieved complete mineralization of PFOA. Direct photolysis at 222 nm far-UVC was also shown to degrade a wide range of PFAS including perfluorocarboxylates (PFCAs), FTUCAs, and GenX.



$\bullet\text{OH}$, with an oxidation potential of 1.9–2.7 V vs. NHE, does not directly cleave C–F bonds or abstract hydrogen from fluorinated carbon chains. Instead, $\bullet\text{OH}$ only participates in secondary transformation of perfluoroalkyl radicals, contributing marginally to chain shortening but not to defluorination. For example, bare TiO_2 systems generate abundant $\bullet\text{OH}$ but achieve less than 21% PFOA defluorination, far lower than reductive systems under similar conditions [53]. Therefore, $\bullet\text{OH}$ -dominated advanced oxidation processes are not recommended as primary defluorination strategies. $^1\text{O}_2$ has been proposed as a reactive species in PFAS degradation. Zhou et al. [54] reported that sulfur-vacancy-engineered ZnIn_2S_4 generates $^1\text{O}_2$ as the dominant reactive oxygen species and correlated its presence with PFOA degradation by EPR and quenching experiments. However, such evidence establishes only a correlation, not a causal role for $^1\text{O}_2$ in C–F cleavage. As an electrophilic oxidant, $^1\text{O}_2$ typically reacts with electron-rich substrates (e.g., alkenes, dienes) or via electron transfer from easily oxidizable groups, whereas the perfluoroalkyl chain has an extremely low HOMO and lacks accessible electron-rich sites for such reactions [55]; electron transfer from perfluoroalkyl carboxylates or sulfonates to $^1\text{O}_2$ is therefore thermodynamically unfavorable, and no direct kinetic evidence for $^1\text{O}_2$ -mediated C–F cleavage has been reported. Consistent with this, conventional triplet photosensitizers (e.g., rose bengal, methylene blue) under visible light have not been shown to achieve significant PFAS defluorination. Thus, $^1\text{O}_2$ may participate in secondary reactions such as headgroup oxidation or intermediate transformation [56], but direct C–F bond cleavage by $^1\text{O}_2$ lacks unambiguous experimental support.

In addition, Hsieh et al. [57] demonstrated that acid-activated h-BN mediates the conversion of ubiquitous Cl^- into chlorine radicals ($\text{Cl}\bullet$) under UVC irradiation. As a strong oxidative species, $\text{Cl}\bullet$ enhanced the degradation rate of PFOA by 2–3 times and increased defluorination efficiency by ~60%, without generating toxic byproducts such as chlorate.

Collectively, while oxidative species play indispensable roles in headgroup activation and chain shortening, their inability to directly cleave C–F bonds, combined with their susceptibility to steric hindrance and matrix effects, limits their standalone defluorination efficiency. This inherent limitation motivates the development of integrated redox strategies (discussed in Section 2.2.3) that leverage the complementary strengths of oxidative and reductive pathways.

2.2. Photocatalytic Defluorination Pathways for PFAS

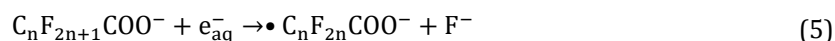
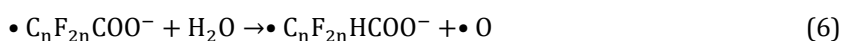
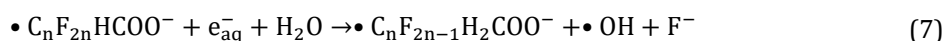
Defluorination efficiency, defined as the molar ratio of released fluoride ions (F^-) to the total fluorine content in the parent PFAS molecule, is a critical metric for evaluating the true mineralization potential of photochemical treatment systems. While numerous studies report high degradation efficiencies of parent PFAS compounds, the corresponding defluorination efficiencies often remain substantially lower, indicating the accumulation of partially fluorinated intermediates. This section systematically compares the dominant defluorination pathways with a focus on their kinetic and thermodynamic characteristics, defluorination efficiency, and the toxicity of transformation products.

2.2.1. Photocatalytic Reductive Defluorination Pathway

The reductive pathway proceeds through two distinct mechanisms: H/F exchange and the DHEH (decarboxylation–hydroxylation–elimination–hydrolysis) chain-shortening route, which differ fundamentally in their reaction intermediates and defluorination efficiencies.

H/F Exchange Mechanism

Reductive attack preferentially occurs at the α -position C–F bond adjacent to the headgroup due to the inductive effect, leading to sequential H/F exchange (Equations (5)–(7)) [26,58].



As illustrated in Figure 1a, attack by a single hydrated electron on one C–F bond generates a carbon-centered radical that abstracts H from water (single H/F exchange); simultaneous attack on two adjacent C–F bonds yield a diradical, which either undergoes a second H/F exchange (forming $-\text{CH}_2-$) or eliminates two fluorides to form a C=C double bond. However, C–H bonds formed in the transformation products strengthen the residual C–F bonds and thus prevent complete defluorination. Theoretical calculations of C–F bond dissociation energies (BDEs) for PFCA and PFSA intermediates reveal that each successive H/F exchange significantly increases the BDE of the remaining C–F bonds, particularly when the newly formed C–H bond is adjacent to a C–F bond (Figure 1b) [59]. This thermodynamic barrier explains the observed defluorination plateau (~55% for C_2 – C_{10} PFCAs) and the accumulation of partially hydrogenated intermediates such as $\text{C}_n\text{F}_{2n}\text{H}-\text{COOH}$, which may be more bioaccumulative and toxic than their fully fluorinated parents [26]. Kinetic studies show that reductive defluorination of PFCAs is diffusion-controlled and nearly chain-length independent, with second-order rate constants of $\sim 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [27]. For PFASs, however, defluorination rates decrease significantly with shorter chain length: the pseudo-first-order rate constant for PFBS is only 13% of that for PFOS in UV/I $^-$ systems [28], reflecting higher C–F BDEs in shorter chains and the lower electron affinity of the sulfonate headgroup.

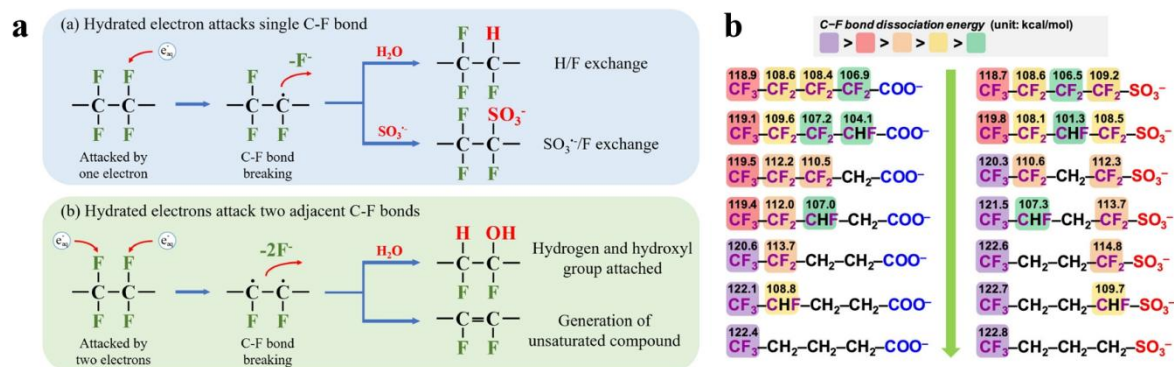


Figure 1. (a) Proposed reaction mechanism of hydrated electrons with a single C-F bond and two adjacent C-F bonds in the UV/sulfite system [60]. (b) Change of calculated C-F BDEs of theory for H/F exchange intermediates from PFCA and PFSA without chain-shortening [59].

DHEH Mechanism

In contrast to H/F exchange, the DHEH pathway avoids hydrogen incorporation into the fluorocarbon chain, enabling stepwise CF₂ removal with near-complete defluorination. This pathway typically initiates with electron attack on the headgroup, followed by decarboxylation for PFCAs or desulfonation for PFSA, and then sequential hydroxylation, HF elimination, and hydrolysis—removing one CF₂ unit per cycle (Equations (8)–(12)) [59,61]. The experimental observation that trifluoroacetate (CF₃COO⁻) achieved 100% defluorination, while difluoroacetate (CF₂HCOO⁻) and monofluoroacetate (CFH₂COO⁻) plateaued at 78% and 57%, respectively, provided critical evidence that the DHEH pathway—rather than stepwise H/F exchange—is essential for deep defluorination [26]. For perfluorodicarboxylates (–OOC–C_nF_{2n}–COO⁻), the presence of two carboxylate headgroups enables defluorination from both ends of the molecule, increasing the overall defluorination efficiency to ~67%, consistently higher than that of monocarboxylates, because the molecule lacks a terminal –CF₃ group that would otherwise act as a recalcitrant endpoint.

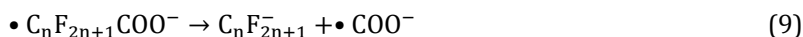
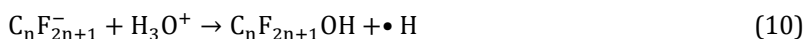


Figure 2 illustrates representative DHEH pathways across different PFAS classes. For short-chain perfluorobutane sulfonate (PFBS), e_{aq}^- cleaves the C-S bond, generating a perfluoroalkyl radical that undergoes hydroxylation, HF elimination, and hydrolysis to yield a PFCA one carbon shorter, which then continues the cycle (Figure 2a) [62]. In CdS nanocrystal systems under visible light, Auger recombination-produced e_{aq}^- triggers C-S cleavage of PFOS, with PFOA as an intermediate, leading to complete defluorination (Figure 2b) [33]. For short-chain PFCAs such as pentafluoropropionic acid (PFPrA), decarboxylation and DHEH produce trifluoroacetic acid (TFA), which achieves 100% defluorination via the same cycle (Figure 2c,d) [62]. Figure 2e compares PFCA and PFSA pathways in a UV reductive system [26]: PFCAs follow two competing routes—H/F exchange (leading to recalcitrant products) and DHEH (chain-shortening with F⁻ release). PFSA, by contrast, primarily undergo C-S bond cleavage—a process with a significantly higher activation barrier than decarboxylation—followed by conversion to PFCAs, which then enter the DHEH cycle. This sequential pathway explains why PFSA exhibit slower degradation kinetics and lower overall defluorination efficiencies than PFCAs of comparable chain length, as the initial C-S cleavage step becomes the rate-limiting stage. The balance between these routes dictates the overall defluorination efficiency (~55% for long-chain PFCAs, ~67% for PFdicarboxylates). These findings highlight that the direct linkage between the fluoroalkyl chain and –COO⁻ is critical for efficient DHEH-driven defluorination.

In summary, H/F exchange introduces C-H bonds that increase residual C-F bond strength, leading to incomplete defluorination and potentially toxic intermediates. In contrast, the DHEH mechanism avoids hydrogen incorporation, enabling near-complete, stepwise CF₂ removal. However, the efficiency of DHEH declines for long-chain congeners due to the higher energy barrier for initial decarboxylation, and the practical

application of both pathways is constrained by the need for strictly anoxic, alkaline conditions ($\text{pH} > 10$) to sustain e_{aq}^- generation [63].

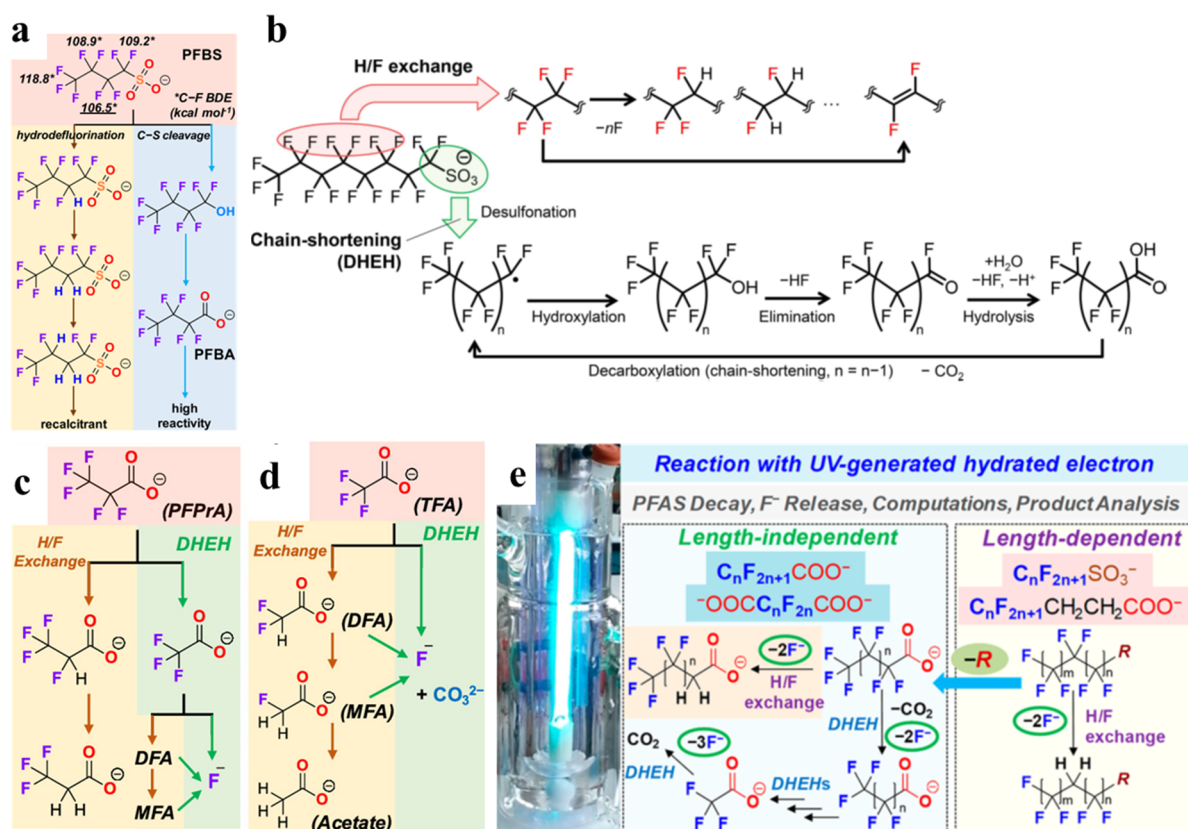
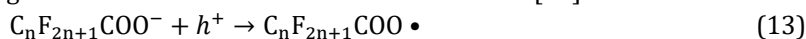
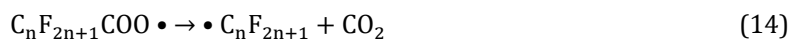
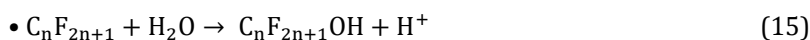


Figure 2. (a) Reaction schemes of short-chain PFBS [62]. (b) Plausible decomposition mechanism of PFOS by visible light irradiation to CdS NCs [33]. Copyright © 2024 Wiley-VCH GmbH. Reaction schemes of short-chain PFPrA (c) and TFA (d) [62]. (e) Comparison of degradation pathways for PFCAs and PFSA in the UV reductive system [26].

2.2.2. Photocatalytic Oxidative Defluorination Pathways

Oxidative defluorination primarily relies on photogenerated holes (h^+) and oxidizing radicals such as sulfate ($\text{SO}_4^{\bullet-}$) and hydroxyl ($\bullet\text{OH}$) radicals, which initiate degradation by extracting electrons from electron-rich sites of PFAS molecules, particularly carboxylate ($-\text{COO}^-$) or sulfonate ($-\text{SO}_3^-$) headgroups.

Generally, the process of PFCAs oxidation defluorination begins with Kolbe decarboxylation, forming a perfluoroalkyl radical (Equations (13) and (14)), which subsequently reacts with $\bullet\text{OH}$ or H_2O to yield an unstable alcohol ($\text{C}_n\text{F}_{2n+1}\text{OH}$) (Equation (15)). This intermediate undergoes HF elimination and hydrolysis (Equations (16) and (17)), producing a short-chain PFCAs with one fewer CF_2 unit [64].



h^+ and O_2^- act as the primary oxidants, initiating Kolbe decarboxylation of PFOA and driving a cyclic chain-shortening mechanism that removes one CF_2 unit per cycle, while $\bullet\text{OH}$ play a negligible role [65]. A similar h^+ and O_2^- -dominated mechanism is observed for PFOS, where the sulfonate group is first cleaved to generate perfluoroalkyl radicals, followed by conversion to PFOA and subsequent stepwise defluorination [66].

A homogeneous advanced oxidation system dominated by $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$: $\text{SO}_4^{\bullet-}$ acts as the initiator by abstracting an electron from the head group via single-electron transfer, whereas $\bullet\text{OH}$ controls the overall degradation rate by attacking key intermediates such as $\text{C}_6\text{F}_{13}\text{COF}$ [67]. In addition, a catalytic ozonation

system where multiple reactive oxygen species ($^1\text{O}_2$, $\bullet\text{OH}$, $\text{O}_2\bullet^-$) coexist with high-valence Fe(IV), creating a synergistic radical-non-radical network. Here, $^1\text{O}_2$ contributes most to defluorination, followed by $\bullet\text{OH}$ and $\text{O}_2\bullet^-$, and the non-radical electron transfer further accelerates the oxidative attack [68]. Such synergistic oxidation systems achieve higher defluorination rates compared to single-oxidant systems, although complete mineralization to fluoride and CO_2 remains challenging.

Despite achieving high parent compound degradation, the overall defluorination efficiency in oxidative systems is typically low. For instance, UV/persulfate treatment of PFOA achieved 100% degradation but only 73.8% defluorination after 12 h [48]. Similarly, BiOCl nanosheets under UV irradiation showed 100% PFOA degradation but only 59.3% defluorination [69]. This discrepancy arises because the oxidative pathway preferentially cleaves C–C bonds rather than C–F bonds, releasing CO_2 but retaining fluorine in short-chain products. Moreover, the α -position CF_2 group adjacent to the carboxylate is most susceptible to attack, while mid-chain C–F bonds remain intact due to steric and electronic hindrance [70]. Consequently, oxidative defluorination is kinetically sluggish and thermodynamically limited, with apparent rate constants for PFOA defluorination in UV/ TiO_2 systems ranging from 0.02 to 0.16 h^{-1} [45,71]. Notably, perfluorosulfonates (PFSAs) like PFOS are even more resistant to oxidative attack due to the higher electron-withdrawing nature of the sulfonate group, requiring prior desulfonation to generate PFCAs before further degradation [72]. The accumulation of short-chain PFCAs (e.g., PFBA, PFPeA) in oxidative effluents raises toxicity concerns, as these compounds remain persistent and mobile in aquatic environments [61].

2.2.3. Oxidative-Reductive Synergistic Defluorination Pathway

Single oxidative or reductive systems suffer from inherent limitations: oxidative systems produce persistent short-chain PFAS intermediates, while reductive systems accumulate hydrofluorinated byproducts, both resulting in incomplete defluorination. Oxidation-reduction synergy overcomes these bottlenecks by combining headgroup activation/chain shortening and direct C–F cleavage, achieving synchronous degradation and complete defluorination.

Liu et al. [59] developed an integrated oxidation–reduction–oxidation strategy. As illustrated in Figure 3, the first oxidative step employs $\bullet\text{OH}$ generated from heat-activated persulfate under alkaline conditions. $\bullet\text{OH}$ attacks the C–H bonds in the ethylene linker, triggering a cascade that converts fluorotelomers into a mixture of PFCAs of all chain lengths. Importantly, this pre-oxidation not only cleaves a substantial portion (35–95%, depending on chain length) of C–F bonds but also transforms the recalcitrant fluorotelomers into PFCAs, which are highly susceptible to subsequent reductive defluorination. The second step uses UV/sulfite to generate e_{aq}^- , which further defluorinates the PFCA mixture to a deep extent (up to ~90%). A final oxidative post-treatment then cleaves the remaining C–F bonds in H-rich residues, achieving near-quantitative overall defluorination (97–103%) for most PFAS structures. This integrated scheme demonstrates that sequential oxidation and reduction can overcome the intrinsic recalcitrance of fluorotelomers.

For the particularly persistent short-chain perfluoroalkyl substance TFA, Mostafavi's group [73] discovered an alternative synergistic pathway involving the nucleophilic oxygen radical anion ($\text{O}\bullet^-$), the deprotonated form of $\text{HO}\bullet$. Under alkaline radiolysis conditions, $\text{O}\bullet^-$ oxidizes TFA with a rate constant of $5.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ —50-fold higher than that of e_{aq}^- —forming a key intermediate $\text{CF}_3\text{CO}_3\bullet^{2-}$. This intermediate undergoes decarboxylation followed by reductive defluorination by e_{aq}^- , leading to complete mineralization of TFA into F^- and CO_3^{2-} without any added catalyst. Extending the synergistic pathway to complex aqueous film-forming foam (AFFF), a tandem UV/sulfite–electrochemical oxidation (UV/S-EO) system uses e_{aq}^- to induce hydrodefluorination, and then applies electrochemical oxidation to mineralize persistent hydrofluorinated intermediates, achieving $\geq 99\%$ defluorination for PFOA, PFOS, and PFBA within 4 h [74]. These synergistic systems leverage the complementary strengths of oxidative C–C bond cleavage and reductive C–F bond scission, resulting in higher overall defluorination rates and lower accumulation of toxic intermediates [75].

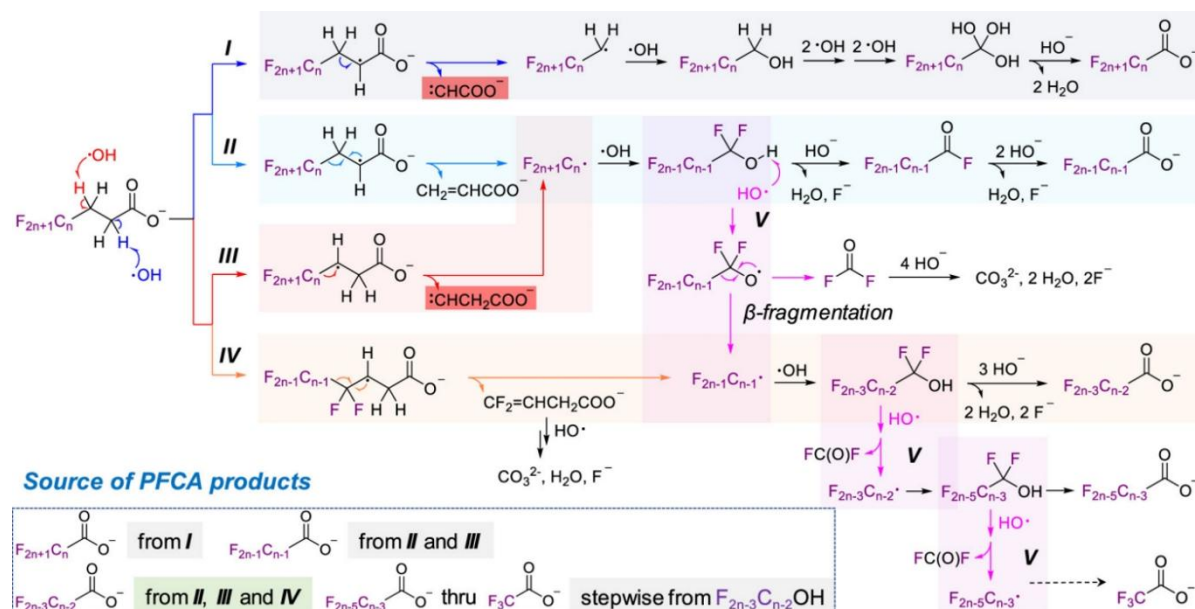


Figure 3. Proposed mechanisms for the generation of PFCAs in all chain lengths from fluorotelomers [59].

Beyond sequential tandem configurations, integrated photoelectrochemical systems offer a powerful platform that intimately couples oxidative and reductive processes for synergistic PFAS defluorination. Fu et al. developed a supercapacitor-assisted electrophotocatalytic system, wherein photochemical reduction by an organic photoreductant is synergistically reinforced by electrochemical activation, achieving 96% defluorination of PTFE under mild, solar-driven conditions without excess sacrificial donors [76]. More recently, Guan et al. reported a Pd-decorated TiO₂ cathode system that enables rapid PFOS defluorination through a dual-electron pathway (hot electrons and hydrated electrons), while the concomitant anodic oxidation further mineralizes persistent intermediates; this oxidative–reductive synergy ensures deep defluorination even in complex matrices such as reverse osmosis concentrate and AFFF-impacted water, with scalable single-chamber reactor designs demonstrated [77].

In summary, oxidative pathways achieve high parent compound degradation but low defluorination efficiency, leaving behind short-chain PFCAs that remain persistent and bioaccumulative. Reductive H/F exchange offers higher defluorination efficiency but generates hydrofluorinated intermediates with potentially enhanced toxicity. The DHEH and synergistic pathways provide the highest defluorination efficiency and deepest mineralization but require complex system design and rigorous control of reaction conditions.

3. Influence Factor and Regulation Strategies for Photocatalytic PFAS Defluorination

The defluorination efficiency is the most critical metric for evaluating the true destruction of PFAS because incomplete degradation may generate persistent short-chain fluorinated intermediates. A variety of interrelated factors govern the defluorination performance in photocatalytic systems, which can be categorized into two distinct groups: objective influencing factors that define the inherent constraints of the system (PFAS molecular structure, solution pH, and water matrix composition), and adjustable operating parameters that can be proactively optimized (light source characteristics, catalyst loading, initial PFAS concentration, and temperature). This section systematically discusses the former—the intrinsic factors that dictate the fundamental feasibility and efficiency of defluorination under given conditions—while the latter are addressed in Section 4.5 as part of the rational design and operational optimization framework. Table 1 summarizes the key experimental parameters and defluorination performance of representative photocatalytic PFAS studies.

Table 1. Summary of representative photocatalytic PFAS defluorination studies and key experimental parameters.

Catalyst/System	PFAS	Initial Concentration	Catalyst Loading	pH	Atmosphere	Light Source	Irradiation Time	Degradation Efficiency	Defluorination Efficiency	Ref.
UV/Sulfite + Iodide	PFBS (C4)	0.025 mM	10 mM Na ₂ SO ₃ , 2 mM KI	12	Air	18 W low-pressure Hg lamp, 254 nm	24 h	>99%	78%	[62]
	PFOA (C8)	0.025 mM					1 h	>99%	88%	
	PFOS (C8)	0.025 mM					24 h	>99%	92%	
	TFA (C2)	0.025 mM					1 h	>99%	100%	
	PFOA	0.25 mM					12 h	~100%	84%	
TiO ₂	PFOA (C8)	50 mg L ⁻¹	0.66 g L ⁻¹	<3	O ₂	16 W low-pressure Hg lamp, 254 nm, 0.45 mW/cm ²	7 h	>99%	38%	[78]
	PFNA (C9)							>99%	54%	
	PFDA (C10)							>99%	38%	
UV/Indole	PFOA	10 mg L ⁻¹	1 mM	6	Air	36 W low-pressure Hg lamp, 254 nm	8 h	100%	74.8%	[23]
CTAB micelle	PFOS	0.025 mg L ⁻¹	0.6 mM	11	N ₂	450 W medium-pressure Hg lamp, 254 nm	2 h	100%	70.8%	
	PFOS							>99%	93%	
	PFOA							>99%	56%	
	PFBS							>99%	83%	
	TFA							100%	100%	[79]
UV/Sulfite	PFOA	32 μM	10 mM	9.2	Air	250 W high-pressure Hg lamp	10 min	99%	-	[21]
	PFOS						60 min	98%	70%	
UV/persulfate	PFOA	1.35 mM	Na ₂ S ₂ O ₈ (50 mM)	3.0	Air	200 W Xe-Hg lamp (220–460 nm)	12 h	100%	73.8%	[48]
UV/Fe(NO ₃) ₃	PFOA	5 ppm	Fe(NO ₃) ₃ (10 mM)	2.4	Air	23 W low-pressure Hg lamp, 254 nm	4 h	100%	~96.8%	[51]
TiO ₂ (P25)	PFOA	5 mM	1.5 wt %	-	Air	Medium-pressure UV lamp, 254 nm, 600 mW/cm ²	4 h	100%	25–38%	[53]
F-TiO ₂	PFOA	50 ppm	0.7 g L ⁻¹	7	Air	11 W UVC lamp, 254 nm, 1.59 mW/cm ²	16 h	92%	~73%	[80]
BiOCl nanosheets	PFOA	20.0 μM	0.5 g L ⁻¹	4.8	O ₂	10 W low-pressure Hg lamp, 254 nm	12 h	100%	59.3%	[69]
BiOCl (OV-rich)	PFOA	20.0 μM	1 g L ⁻¹	4.6	Air	10 W low-pressure Hg lamp, 254 nm	8 h	100%	59.6%	[81]
BiOCl/TiO ₂	PFOA	10 mg L ⁻¹	0.1 g L ⁻¹	natural	Air	254 nm UV (or Xe lamp)	8 h	96%	82%	[82]
In-MOF/BiOF	PFOA	15 mg L ⁻¹	0.5 g L ⁻¹	-	Air	500 W Hg lamp (UV)	2.5 h	100%	34%	[83]
CuInS ₂ /BiOCl	OBS	30 mg L ⁻¹	1.25 g L ⁻¹	6.36	Air	UV (20 W, 254 nm)	8 h	100%	75.8%	[84]
CdS NCs	PFOS	1.2 mM	0.8 mg	7	N ₂	LED, 405 nm, 830 mW/cm ²	8 h	100%	100.9%	[33]
	Nafion powder, -SO ₂ F form	24 h					-	1.8%		
	Nafion saponified, -SO ₃ ⁻ form	24 h					-	81%		
	PTFE	48 h					-	5%		
ZnO NCs	PFOS	~1.2 mM	5 g L ⁻¹	10	N ₂	LED, 365 nm, 868 mW/cm ²	24 h	>99%	92%	[37]
Ga/TNTs@AC	PFOS (surface water)	100 μg L ⁻¹	1 g L ⁻¹	3.5	Air	UV, 254 nm, 210 W/m ²	4 h	80.4%	70.0%	[85]
BPI + nBu ₄ NF	PFOA	0.05–0.1 M	2.0 mol%	-	N ₂	390 nm LED	24 h	89%	-	[40]
	PFOS	0.05–0.1 M						~60%	-	
KQGZ	PTFE	-	2 mol%	-	Ar	407 nm LED, 54 W	48 h	-	96%	[38]
	PFOS	~0.2 M					24 h	-	60%	
	PFOA	~0.2 M					24 h	-	60%	
TAPP	PFOS	0.1 ppm	0.2 g L ⁻¹	-	Air	Visible light (λ ≥ 420 nm)	48 h	>99%	99.8%	[86]
BT-FI-Py	PFOA	0.05 ppm	0.2 g L ⁻¹	-	Air	Visible light (λ ≥ 420 nm)	30 h	~100%	~100%	[87]

3.1. PFAS Molecular Structure

The molecular architecture of PFAS, including perfluoroalkyl chain length, head group type, and the presence of ether linkages or branching, determines the bond dissociation energies and single-electron reduction potentials of C–F bonds at different positions (Figure 4a,b), and also profoundly affects their adsorption affinity, reactivity with photogenerated species, and ultimately the defluorination efficiency.

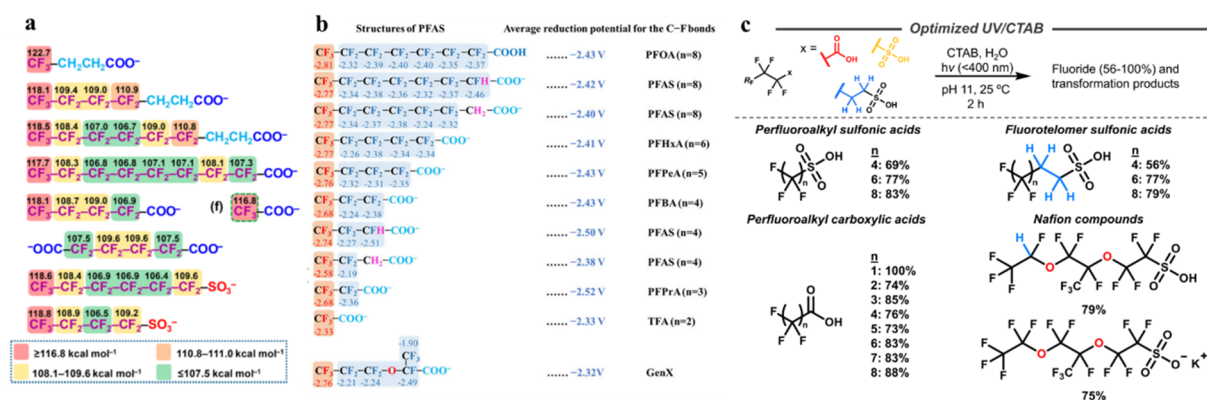


Figure 4. (a) BDE for all the C–F bonds in PFASs [26]. (b) One-electron reduction potential for all the C–F bonds in PFASs. Adapted with permission from Ref. [30]. Copyright © 2025, American Chemical Society. (c) Fluoride recovery from the optimized UV/CTAB system for several structure classes. Adapted with permission from Ref. [79]. Copyright © 2025, American Chemical Society.

3.1.1. Chain Length

Long-chain PFCAs (C ≥ 7) generally exhibit higher defluorination efficiencies than short-chain homologues under identical photocatalytic conditions. This is primarily attributed to stronger hydrophobic interactions between the long perfluoroalkyl tail and the catalyst surface, which facilitates pre-concentration and subsequent attack by reactive species. For example, in a UV/sulfite reductive system, the apparent defluorination rate constants decreased markedly with shortening chain length: PFOA (C8) showed a pseudo-first-order defluorination rate constant of 0.162 h⁻¹, while PFBA (C4) was degraded much more slowly and achieved only ~20% defluorination after 24 h [62]. Similarly, in a UV/TiO₂ photocatalytic system, the decomposition of PFCAs followed the order PFDA (C10) > PFNA (C9) > PFOA (C8) > PFHpA (C7), with defluorination decreasing from ~54% for PFNA to ~38% for PFOA after 6 h of irradiation [78].

In particular, high-molecular-weight perfluorinated polymers, most notably polytetrafluoroethylene (PTFE), represent an extreme case in terms of photocatalytic recalcitrance. With its ultra-long, fully fluorinated carbon backbone and complete absence of any functional head group, PTFE is exceptionally inert and does not obey the structure–reactivity patterns established for smaller PFAS molecules. Its complete insolubility in water and most organic solvents, coupled with an extremely negative reduction potential (below –3.0 V vs. SCE), renders it impervious to traditional photocatalysts and aqueous-phase reduction systems. For decades, the only viable methods for PTFE defluorination required either extremely high temperatures (>500 °C) or the use of powerful, hazardous chemical reducing agents like alkali metals in liquid ammonia. A breakthrough was achieved using the organic super-photoreductant KQGZ [38], which enabled low-temperature (40–60 °C) defluorination in DMSO under 407 nm light, yielding 96% fluoride as KF and amorphous carbon. The reaction does not rely on e_{aq}⁻ in the aqueous phase but rather on a direct, surface-mediated electron transfer, circumventing the solubility and redox potential barriers that had previously made PTFE undegradable under photocatalytic conditions.

3.1.2. Head Group

Carboxylate-terminated PFAS (PFCAs) are generally more amenable to photocatalytic defluorination than sulfonate-terminated ones (PFSAs). The terminal functional group of a PFAS molecule is critical in determining its susceptibility to photocatalytic attack, particularly in oxidative systems. PFCAs, with their terminal carboxylate group (–COO⁻), are generally more readily degraded by photogenerated h⁺ than PFSAs, which have a sulfonate head group (–SO₃⁻). This is because the carboxylate group can be directly oxidized via a photo-Kolbe decarboxylation reaction, a key initial step that generates a perfluoroalkyl radical and

triggers chain-shortening. In contrast, sulfonate groups require initial C–S bond cleavage, which has a substantially higher activation barrier, before the perfluoroalkyl chain can undergo further degradation.

This fundamental difference was first demonstrated by Hori et al., who showed that UV/persulfate treatment completely decomposed PFOA within 4 h with an initial rate 11 times faster than direct photolysis, whereas PFOS was markedly less reactive under similar conditions [47,48]. The superior reactivity of PFCAs is further evidenced in reductive systems: Qu et al. achieved 98% defluorination of PFOA within 24 h using UV/iodide at pH 9 [22], while Park et al. reported only ~55% defluorination for PFOS under comparable conditions [25]. In semiconductor photocatalysis, Li et al. demonstrated that In_2O_3 achieves complete PFOA decomposition with a rate constant ~8.4 times higher than TiO_2 , attributed to bidentate coordination between the carboxylate headgroup and the catalyst surface, which facilitates direct hole oxidation [45]. The structural origin of this reactivity disparity was systematically confirmed by Bentel et al., who examined 34 PFAS structures and found that the direct linkage between the fluoroalkyl chain and the carboxylate headgroup ($-\text{COO}^-$) is critical for rapid defluorination via the DHEH pathway, whereas sulfonates exhibit consistently lower defluorination efficiencies due to the higher energy barrier for C–S cleavage [26]. Yang et al. further compared the defluorination of PFOA and PFOS using heat-activated persulfate and found that PFOS was first converted to PFOA via attack on the C–S bond, and only then followed the same stepwise defluorination pathway, resulting in slower overall defluorination kinetics [72]. Consequently, the reactivity order PFCAs > PFASs holds across diverse oxidative, reductive, and photocatalytic systems, underscoring the intrinsic structural basis—direct decarboxylation versus rate-limiting desulfonation—rather than system-specific effects.

3.1.3. Ether Linkages and Branching

Emerging PFAS alternatives containing ether oxygens and branched $-\text{CF}_3$ groups, exhibit distinct defluorination behaviors depending on the dominant reactive species. In oxidative UV/persulfate systems, GenX (HFPO-DA) showed much poorer defluorination (<5% in 3 h) compared to PFOA (~27%), because the $\alpha\text{-CF}_3$ group sterically hinders $\text{SO}_4^{\bullet-}$ attack on the carboxylate head. In contrast, under reductive UV/sulfite system, GenX became undetectable in 2 h with >90% defluorination after 6 h, because the ether bond serves as a favorable attack site for e_{aq}^- , and its defluorination even exceeded that of PFOA [49]. Similarly, C7 HFPO-TA with a unique $\text{CF}_3\text{O}-\text{CF}(\text{CF}_3)-$ fragment, including two ether bonds and two branched $-\text{CF}_3$ groups, was further investigated by Huang's group [88]. Under $\text{SO}_4^{\bullet-}$ oxidation, its decay was only 65.0% (vs. 82.0% for PFOA) and defluorination 30.3% after 480 min, again due to $\alpha\text{-CF}_3$ steric hindrance. Under e_{aq}^- reduction, decay and defluorination increased to 91.1% and 56.6%, respectively, but remained lower than PFOA because most C–F bonds were more recalcitrant and H/F exchange intermediates strengthened adjacent C–F bonds. Notably, under synergistic treatment with both $\text{HO}^\bullet$ and e_{aq}^- , C7 HFPO-TA achieved 99.9% decay and 81.5% defluorination, with a unique H/OCF₃ exchange pathway enabled by the branched $-\text{CF}_3$ attached directly to the same carbon next to the $\text{CF}_3\text{O}-$ group. This shifted the ether C–O cleavage site from $\text{CF}_3\text{O}-$ to $\text{CF}_3\text{O}-\text{C}$, as confirmed by DFT (BDE of $\text{CF}_3\text{O}-\text{C}$ dropped from 91.7 to 81.4 kcal mol⁻¹). Comparing four PFECAs under synergistic $\bullet\text{OH}/e_{\text{aq}}^-$ treatment, the defluorination order was C7 HFPO-TA > GenX > HFPO-TA > HFPO-TeA, proving that defluorination is highly structure-dependent: ether bonds aid reducibility, but $\alpha\text{-CF}_3$ branches severely hinder oxidation, and the relative position of branches and ether oxygens can create entirely new degradation mechanisms.

In the UV/CTAB micellar system, defluorination efficiency varies significantly with PFAS structure. As shown in Figure 4c, long-chain PFOS (C8) achieve >90% fluoride recovery within 2 h, while short-chain PFBS (C4) reaches only 56% due to weaker hydrophobic interactions with the micelle. The presence of an ethylene linker ($-\text{CF}_2\text{CF}_2-$) in 4:2 FTSA lowers defluorination compared to PFBS with the same fluorocarbon chain length, as adjacent C–H bonds stabilize C–F bonds. Perfluoroether sulfonates (PFESAs) are also effectively degraded, leaving no more than four C–F bonds. In contrast, trifluoromethanesulfonate (CF_3SO_3^-) and 1:1 trifluoroethanesulfonate ($\text{CF}_3\text{CH}_2\text{SO}_3^-$) show negligible defluorination, indicating that isolated $-\text{CF}_3$ and C–S bonds are inert to hydrated electrons. However, trifluoroacetate (CF_3COO^-) is completely defluorinated, highlighting the critical role of the carboxylate group in activating the CF_3 moiety [79].

3.2. Solution pH

Solution pH strongly influences the surface charge of photocatalysts, the speciation of PFAS (always anionic at environmentally relevant pH due to very low pK_a), and the formation/scavenging of reactive species, thereby directly impacting defluorination efficiency.

3.2.1. Acidic Regulation for Oxidative Pathways

For h^+ -mediated photocatalysis (e.g., TiO_2 , BiOCl , In_2O_3), acidic conditions (pH 2~4) consistently favor higher defluorination. Under low pH, the catalyst surface is positively charged, enhancing electrostatic attraction with anionic PFAS. Moreover, h^+ is more abundant because the competing reaction with OH^- is suppressed. For instance, in a BiOCl nanosheet system, PFOA defluorination reached 59.3% after 12 h at pH 2.5, but decreased to 41% at pH 7.1 and to only 12% at pH 11 [69]. Similarly, Chen et al. reported that Pb-doped TiO_2 achieved 22.4% defluorination of PFOA at pH 3.0, whereas the value dropped to <10% at pH 9.0 [89]. In addition, Song et al. reported that pH affects PFOA defluorination by modulating the electrostatic interaction between PFOA and the BiOCl surface, as the pK_a of PFOA (2.8) coincides with the catalyst's point of zero charge (2.8); optimal defluorination occurred near pH 3.0, while stronger acidity or alkalinity suppressed the performance due to unfavorable surface charging and PFOA speciation [81].

3.2.2. Alkaline Regulation for Reductive Pathways

In e_{aq}^- -based systems, high pH (typically 9~12) is essential for efficient defluorination because H^+ ions rapidly scavenge e_{aq}^- [90]. Song et al. studied PFOA degradation by UV/sulfite and observed that the defluorination efficiency dropped sharply from 88.5% to nearly zero as the pH changed from 10.3 to 6.0 [41]. In a UV/iodide system, Qu et al. reported that PFOA defluorination was 98.8% at pH 9.0 under N_2 purging, but nearly ceased at $\text{pH} \leq 5.0$ due to protonation of e_{aq}^- [91].

3.3. Water Matrix Composition

Natural and wastewaters contain various dissolved constituents that can scavenge reactive species, compete for adsorption sites, or attenuate light penetration, often severely suppressing defluorination compared to ultrapure water, thereby directly affecting the application of photocatalytic systems in the environment [85].

3.3.1. Dissolved Oxygen (DO)

DO is the most critical inhibitor for reductive defluorination because O_2 reacts with e_{aq}^- at nearly diffusion-controlled rate ($k = 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). In the UV/sulfite system, the defluorination of PFOA fell from 88.5% under N_2 to just 6.4% under air-saturated conditions [41]. For oxidative systems, DO can sometimes be beneficial by generating $\bullet\text{O}_2^-$, but $\bullet\text{O}_2^-$ itself has limited ability to cleave C–F bonds. Javed et al. demonstrated that $\bullet\text{O}_2^-$ did not contribute significantly to PFOA defluorination in a boron nitride photocatalytic system, and the presence of DO only slightly improved the overall degradation but not defluorination [42].

3.3.2. Natural Organic Matter (NOM)

NOM, such as humic acid, competes for both adsorption sites on the catalyst surface and for photogenerated holes/electrons, resulting in a marked decrease in defluorination. In a UV/iodide reductive system, the addition of 10 mg/L humic acid reduced PFOS defluorination from 55.6% to ~20% within 1.5 h [92]. In a heterogeneous photocatalytic system using In_2O_3 , the presence of 10 mg/L humic acid lowered the PFOA defluorination rate constant from 0.378 h^{-1} to 0.112 h^{-1} [45].

3.3.3. Coexisting Anions

Chloride (Cl^-), bicarbonate (HCO_3^-), nitrate (NO_3^-), and sulfate are common in water and can severely quench reactive species. Cl^- scavenges both h^+ and $\bullet\text{OH}$, forming less reactive chlorine radicals ($\text{Cl}\bullet$, $\text{Cl}_2\bullet^-$). In a UV/persulfate system, adding 100 mM NaCl reduced PFOA defluorination from ~50% to <10% [93]. HCO_3^- reacts with $\bullet\text{OH}$ and h^+ to produce ($\text{CO}_3\bullet^-$), which has a lower oxidation potential (1.78 V vs. NHE) and is less effective for defluorination. In a UV/ TiO_2 system, 10 mM HCO_3^- decreased PFOA defluorination by ~40% [78]. NO_3^- is an extremely efficient e_{aq}^- scavenger ($k = 9.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). In a UV/sulfite system for PFOS degradation, the presence of 0.5 mM NO_3^- reduced the defluorination efficiency from 94% to <20% after 6 h [21].

In addition, cations such as Ca^{2+} , Mg^{2+} can act as bridges between anionic PFAS and negatively charged catalyst surfaces, sometimes enhancing adsorption and thereby improving defluorination. For example, in a Fe-modified titanate nanotube/activated carbon system, the addition of 1 mM Ca^{2+} increased PFOA

adsorption by ~15% and slightly improved the subsequent defluorination rate [94]. However, excessive cations may cause surface fouling.

4. Design Principles and Regulation Strategies for High-Performance Photocatalytic PFAS Defluorination Systems

Photocatalytic defluorination of PFAS is constrained by some challenges, including insufficient visible-light absorption, rapid electron–hole recombination, and low utilization efficiency of photogenerated carriers at the catalyst–solution interface. Addressing these barriers requires a multi-tiered strategy that integrates electronic structure modulation, interface chemistry engineering, light absorption broadening, and macrostructural design. To articulate our design philosophy, we present a conceptual framework (Figure 5) that cascades from PFAS enrichment to interfacial charge transfer and position-dependent C–F bond activation, emphasizing that balanced performance across all tiers governs the ultimate defluorination efficiency.

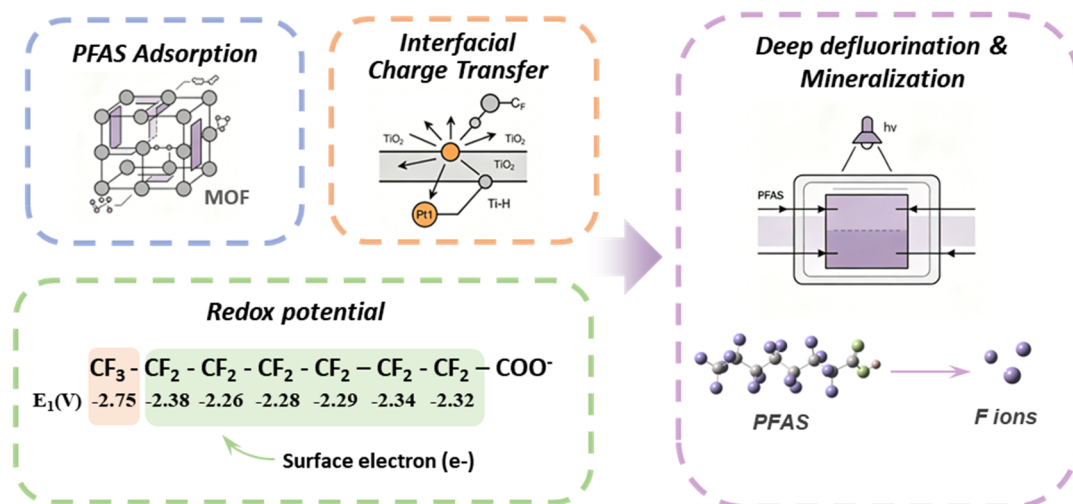


Figure 5. Conceptual cascade design for photocatalytic PFAS defluorination.

4.1. Electronic Structure Modulation

Efficient separation of photogenerated charge carriers and preservation of their strong redox potentials are prerequisites for achieving deep defluorination. Enhancing the yield and lifetime of these species while suppressing charge recombination is therefore the first line of defense in achieving high defluorination efficiency.

4.1.1. Built-in Electric Field Regulation and Heterojunction Engineering

The separation and migration of photogenerated carriers can be significantly enhanced by constructing a built-in electric field at the interface of different materials.

A common strategy is the formation of a Schottky junction between a semiconductor and a metal with a larger work function, which drives electron flow from the semiconductor to the metal and thus suppresses charge recombination. Li et al. decorated TiO₂ with noble metals (Pt, Pd, Ag) having work functions (5.65, 5.55, and 4.26 eV, respectively) higher than that of TiO₂ (4.20 eV) [95,96]. The resulting Schottky barrier drives photogenerated electrons from TiO₂ to the metal, suppressing recombination and leaving more holes for PFOA oxidation. Consequently, the pseudo-first-order rate constants for PFOA degradation over Pt-TiO₂, Pd-TiO₂, and Ag-TiO₂ were 0.7267, 0.4369, and 0.1257 h⁻¹, which are 12.5, 7.5, and 2.2 times higher than that of bare TiO₂, demonstrating a positive correlation between the work function difference and defluorination efficiency [95].

Beyond metal-semiconductor junctions, constructing semiconductor–semiconductor heterojunction represents a core strategy for preserving strong redox potentials while promoting charge separation. These heterojunctions rely on the built-in electric field at the interface to direct charge flow. For instance, in a p–n heterojunction of BiOX/TiO₂, the self-induced internal electric field (IEF) within BiOX layers directs electron migration along [001] to TiO₂, while the built-in electric field (BIEF) at the interface drives hole transfer from TiO₂ to BiOX via the [110] facet. This spatial charge separation greatly suppresses recombination. Consequently, BiOCl/TiO₂ achieves a PFOA defluorination ratio of 82%, far exceeding that

of pure BiOCl (27%) or TiO₂ (negligible), demonstrating that synergistic IEF and BIEF regulation is critical for high-efficiency PFAS defluorination [82]. An n-n heterojunction was constructed between In-MOF and BiOF. Under UV irradiation, photogenerated electrons from BiOF migrate to In-MOF, while holes remain in BiOF, achieving complete degradation of PFOA and PFOS with defluorination efficiencies of 34% and 29%, respectively [83].

Besides, a quintessential example of a Z-scheme heterojunction is zero-dimensional CuInS₂ quantum dots anchored on two-dimensional BiOCl nanoplates (CuInS₂/BiOCl) (Figure 6a). The IEF at the interface drives photogenerated electrons to accumulate in the conduction band of CuInS₂ and holes in the valence band of BiOCl, thereby retaining the strong reducing power of electrons for C–F bond cleavage and the strong oxidizing power of holes for carbon chain scission. This system achieved a remarkable defluorination efficiency of 75.8% and total organic carbon removal of 76.8% for sodium *p*-perfluorooctanesulfonate (OPS) within 8 h under UV irradiation, demonstrating synchronous deep defluorination and mineralization [84]. A direct Z-scheme heterojunction of core-shell CeO₂@NiAl-layered double hydroxides (CeO₂@NiAl-LDHs) was reported to significantly enhance PFOA photodegradation [97]. The formation of the Z-scheme accelerated electron transfer from CeO₂ to NiAl-LDHs, suppressing recombination and boosting the generation of reactive species. Under simulated solar irradiation, CeO₂@NiAl-LDHs achieved 90.2% PFOA removal, substantially outperforming pristine CeO₂ (23.6%) and NiAl-LDHs (55.3%). In addition, a type-II heterojunction of h-BN/Fe₂O₃ directs photogenerated electrons from Fe₂O₃ to h-BN and accumulates holes on h-BN, achieving efficient charge separation. The optimized composite achieves 92% PFOA degradation and 61.7% defluorination in 60 min [98].

4.1.2. Defect Engineering

Oxygen vacancies (OVs) serve a dual function in photocatalytic degradation, including trap photogenerated electrons to suppress charge recombination and create unsaturated coordination sites that enhance PFAS adsorption and facilitate C–F bond activation.

By controlling the amount of ethylene glycol during synthesis, tunable oxygen vacancies were introduced onto the exposed (101) facets of BiOF nanosheets. This defect engineering reduced the bandgap from 3.49 eV to 3.45 eV and created a new intermediate energy band, facilitating electron transition and hole oxidation. The resulting material exhibited a PFOA degradation rate constant ~10 times higher than pristine BiOF [99]. Song et al. [81] systematically controlled the OVs in BiOCl nanosheets and found that as the concentration of OVs increased (from an A(O_M/O_L) ratio of 0.573 to 0.981), the photocatalytic degradation and fluorination removal of PFOA increased by 3 to 4 times, exhibiting a linear relationship between the amount of oxygen vacancies and the fluorination rate constant, and the OVs-rich BiOCl achieved 100% PFOA degradation and 59.6% defluorination after 8 h. In addition, In₂O₃ porous microspheres with abundant surface oxygen vacancies achieved complete decomposition of PFOA within 20 min under 254 nm UV irradiation, outperforming both In₂O₃ nanoplates and nanocubes [100]. Glass et al. [101] doped Fe(III) into hBN via a deep-eutectic-solvent method, introducing Fe–N/Fe–O coordination defects that narrow the bandgap and promote hole localization. The Fe(III) sites electrostatically adsorb PFOA and facilitate direct electron transfer, doubling the defluorination efficiency (>40%) compared to undoped hBN (~20%).

4.1.3. Single-Atom Catalysis

Single-atom catalysts (SACs) represent the theoretical limit of metal dispersion, maximizing atom utilization efficiency and introducing unique electronic properties distinct from nanoparticle counterparts. For PFAS defluorination, SACs offer a particularly attractive pathway: atomic-scale metal centers can activate C–F bonds through mechanisms unavailable to bulk catalysts.

Site-selective loading of single-atom Pt (Pt₁) on facet-engineered TiO₂ enabled efficient hydrodefluorination of PFOA via hydrogen spillover (Figure 6b). Positively charged Pt₁ atomically dispersed on the reductive sites of TiO₂ efficiently attracts photoinduced electrons, enhancing hole availability for oxidation reactions. Unlike Pt nanoparticle cocatalysts that consume electrons for oxygen reduction, site-specifically loaded Pt₁ produces surface hydrogen atoms and enhances hydrogen spillover onto the TiO₂ surface, enabling C–F bond cleavage via Ti–H bond formation. This enabled a hydrodefluorination pathway, achieving ~40% defluorination of PFOA within 2 h under UV irradiation [35]. Likewise, single-atom Pt anchored on SiC (Pt₁/SiC) activated C–F bonds via hydrogen spillover, attaining 50.6% defluorination of PFOA in 1.5 h [102].

From a defluorination efficiency perspective, SACs offer three distinct advantages over conventional catalysts: nearly 100% atom utilization eliminates inactive bulk metal; unique electronic structures at isolated metal sites lower activation barriers for C–F bond scission; and hydrogen spillover effects can be tuned to favor reductive defluorination pathways.

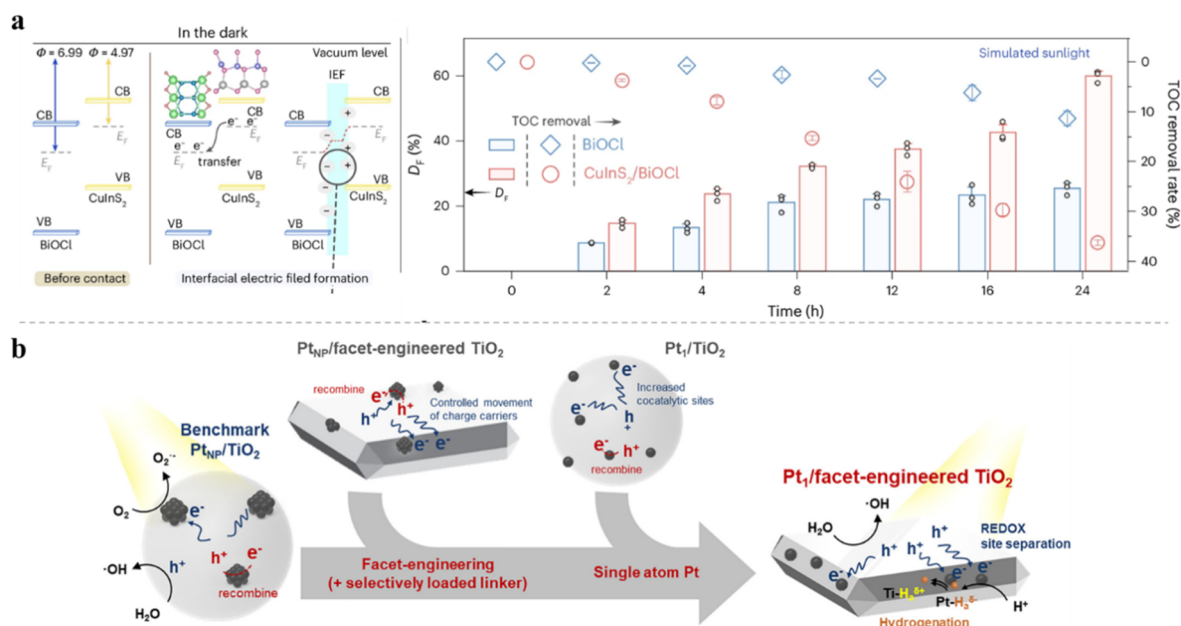


Figure 6. (a) A schematic illustration of the formation of $\text{CuInS}_2/\text{BiOCl}$, and defluorination efficiency and TOC removal rate by BiOCl and $10\text{-CuInS}_2/\text{BiOCl}$ under simulated sunlight [84]. (b) Photocatalysis mechanisms of Pt nanoparticle loaded TiO_2 , Pt single-atom loaded TiO_2 , Pt nanoparticle loaded facet-engineered TiO_2 , and Pt single-atom loaded facet-engineered TiO_2 . Adapted with permission from Ref. [35]. Copyright © 2021, American Chemical Society.

4.1.4. Organic Photoredox Catalysts

Beyond inorganic and hybrid materials, molecular organic super-photoreductants offer an alternative strategy for achieving extreme reducing potentials through excited-state electron transfer. Their electronic structure can be tuned by molecular design, core twisting, donor–acceptor arrangement, or closed-shell formation to populate highly reducing excited states capable of cleaving inert C–F bonds. Nicewicz’s group [39] exploited a twisted intramolecular charge-transfer (TICT) state in a neutral acridine radical ($\text{Mes-Acr}^\bullet$). The rotation of the N-phenyl ring relative to the acridine plane creates a higher-energy doublet excited state with an oxidation potential of -3.36 V vs. SCE, comparable to elemental lithium. This super-reductant efficiently hydrodefluorinates inert aryl fluorides and chlorides via single-electron transfer. Zhu’s group [86] developed TAPP aggregates as visible-light-driven organic photoredox catalysts. Photoexcitation generates an ultra-stable TAPP radical (lifetime >7 days), which undergoes second excitation to produce a highly reductive state (-2.68 V vs. NHE). This enables direct electron injection into C–F antibonding orbitals, achieving 99.8% defluorination of PFOS at 0.1 ppm without any additives, under solar light, with energy consumption as low as 3.99 kWh m^{-3} . Liu et al. [40] demonstrated a closed-shell strategy using benzo[ghi]perylene monoimide (BPI) and nBu_4NF . Fluoride-assisted ring opening followed by photoexcitation generates a closed-shell singlet species (BPI-RO-H_2^-) with a two-electron/one-proton reduced core. Its excited-state reduction potential reaches -3.64 V vs. SCE, the most negative among organic photoreductants, enabling direct C–F bond activation in diverse organofluorines, PFASs, and fluorinated polymers under mild blue light irradiation. Zhang et al. designed a twisted carbazole-cored super-photoreductant, KQGZ, where the large torsional angle between carbazole rings promotes intramolecular charge separation and stabilizes the excited state. Upon deprotonation and photoexcitation, KQGZ exhibits an excited-state oxidation potential of -3.01 V vs. SCE, enabling reductive defluorination of a series of PFASs (PFCs, PFOA, PFOS) and even PTFE at $40\text{--}60^\circ\text{C}$ with up to 96% fluoride yield. Zhu’s group further extended TICT-based photoreductive design to BT-Fl-Py linear conjugated polymers [87]. Upon single-photon excitation under visible light, BT-Fl-Py forms microsecond-lived TICT₁ state with a reduction potential of -1.6 V vs. SCE, delivering sufficient reduction capacity to mineralize PFOA. Benefiting from its

hydrophobic polymer backbone, the catalyst simultaneously enriches aqueous PFAS and maintains outstanding recyclability for practical solar-driven water remediation.

4.2. Interface Chemical Regulation

Even with abundant reactive species, photocatalytic defluorination efficiency remains limited if PFAS molecules cannot access the catalyst surface where these species are generated. The strong hydrophobicity and anionic nature of PFAS demand tailored surface chemistry that promotes both enrichment and activation. Also, given the trace concentrations, hydrophobicity, and anionic nature of PFAS in the environment, tailoring the interfacial microenvironment is crucial for implementing the concentrate-destroy strategy.

4.2.1. Hydrophobic/Hydrophilic balance Regulation

The design of photocatalyst surfaces for PFAS capture must account for the dual nature of these contaminants—a hydrophobic fluorinated tail and a polar anionic head group—and must clearly distinguish between adsorption, degradation, and defluorination, as high removal efficiency does not necessarily indicate chemical destruction of the parent compound.

Fluorine-doped TiO₂ (F-TiO₂) [80] synthesized via one-step PVDF pyrolysis exemplifies this principle (Figure 7a): the material demonstrated enhanced PFOA adsorption through hydrophobic interactions while maintaining charge separation efficiency. Under UVC irradiation (254 nm, 1.59 mW cm⁻²) with sodium persulfate, F-TiO₂ achieved ~92% PFOA removal at 700 mg/L catalyst, compared to ~58% for pristine TiO₂, with a nine-fold faster apparent kinetics (rate constant: 0.217 h⁻¹ vs. 0.024 h⁻¹); ion chromatography analysis confirmed partial defluorination (~25 ppm F⁻ after 16 h irradiation), indicating that a portion of the removed PFOA was chemically destroyed rather than merely adsorbed. Similarly, 3D sulfonated graphene (SG)-TiO₂ quantum dot (QD) aerogels leveraged the hydrophobic surface of 3D SG to instantaneously enrich PFOA (adsorption rate 0.0381 s⁻¹), while the dispersed TiO₂ QDs (2–3 nm) provided photocatalytic decomposition (1.898 × 10⁻⁴ s⁻¹) under a 150 W medium-pressure Hg lamp [103]. Wang et al. [104] further illustrated this principle by comparing hydrophobic BN (contact angle 54°) with hydrophilic TiO₂ (18°) under 254 nm UVC irradiation with a photon flux of 6.5 × 10⁻⁶ Einstein L⁻¹ s⁻¹ and a spectral irradiance of 4.33 mW cm⁻². BN adsorbed approximately twice as much PFOA and exhibited 2.5–3.5-fold faster degradation, with higher defluorination (22% vs. 16%). The enhanced performance of BN was attributed to its greater surface hydrophobicity, which promotes PFOA adsorption and suppresses parasitic hole consumption by water, thereby directing photogenerated holes toward oxidation of adsorbed PFAS. The titanium-based MOF MIL-177-HT further illustrates the importance of ligand hydrophobicity: although its specific surface area was approximately half that of MIL-125-NH₂ (609 m²/g vs. 1202 m²/g) [105], its greater ligand hydrophobicity enabled approximately 83% PFOA removal and 32% defluorination within 24 h under a 450 W medium-pressure Hg-vapor lamp (λ = 185–600 nm). These observations underscore a general design principle: hydrophobic domains are essential for capturing PFAS from water, but must be balanced with sufficient hydrophilicity to ensure water access and efficient charge transfer—and importantly, adsorption must be followed by photocatalytic destruction to achieve true defluorination rather than merely phase transfer.

4.2.2. Surface Charge Modulation

Electrostatic interactions between anionic PFAS head groups and positively charged catalyst surfaces can dramatically enhance both adsorption and degradation. This can be achieved through cationic polymer coatings, metal ion grafting, or tuning the point of zero charge (PZC). For instance, a TiO₂-rGO composite (95% TiO₂/5% rGO) achieved 93 ± 7% PFOA degradation in 12 h under UV-vis, far outperforming bare TiO₂ (24 ± 11%) and photolysis (58 ± 9%). rGO acts as an electron acceptor, suppressing charge recombination and enabling stepwise hydroxyl-radical-mediated decomposition [106]. Metal ion grafting offers another route to surface charge modulation. In the Fe/TNTs@AC composite, the loaded Fe³⁺ not only shifted the PCZ from 2.6 to 5.2 but also coordinated with the carboxylate group of PFOA via Lewis acid–base interactions. Combined with the hydrophobic adsorption by AC, this formed a highly efficient “side-on” adsorption mode, where both the hydrophobic tail (interacting with carbon particles) and the carboxylate head group (interacting with Fe³⁺ sites via Lewis acid–base interactions) contribute to PFAS enrichment (Figure 7b), facilitating subsequent hole-mediated decarboxylation. The system achieved >90% degradation and 62% defluorination of pre-concentrated PFOA within 4 h under UV light [94].

4.2.3. Molecular Imprinting Technology

Molecularly imprinted polymers (MIPs) offer a route to highly selective PFAS capture by creating “shape-memory” cavities that match specific target molecules. When integrated with photocatalysts, MIPs can selectively enrich target PFAS even in complex water matrices containing competing organic matter, thereby maximizing the utilization efficiency of photogenerated carriers. Wu et al. fabricated MIP-modified TiO₂ nanotubes (MIP-TiO₂ NTs) using PFOA as a template. In the presence of competing contaminants (e.g., PFOS), the MIP-TiO₂ NTs maintained a PFOA degradation efficiency of 82.0%, significantly outperforming non-imprinted NTs (60.5%) [107].

4.2.4. Nanoconfinement Effect

Confined nano-spaces act as nanoreactors that enrich PFAS and alter their electronic states, thereby enhancing reactivity. A di-indole hexadecyl ammonium (DIHA) molecule self-assembles into nanospheres (100–200 nm) in water. These nanospheres concentrate PFAS on their surface via electrostatic, hydrophobic, and van der Waals interactions. The confined surface simultaneously generates surface electrons and surface hydroxyl radicals, enabling ~90% defluorination for PFOA and PFOS within 6 h under UV irradiation (Figure 7b) [108]. Beyond self-assembled nanospheres, well-defined metallacages offer another powerful platform for nanoconfinement. A pyrene-based multicomponent metallacages provide a well-defined nanoconfinement platform, exhibiting a high PFOA adsorption capacity of 1223 mg/g via multivalent electrostatic and hydrogen bonding interactions. Upon 365 nm UV irradiation, the pre-concentrated PFOA achieving 91% defluorination in 6 h [94].

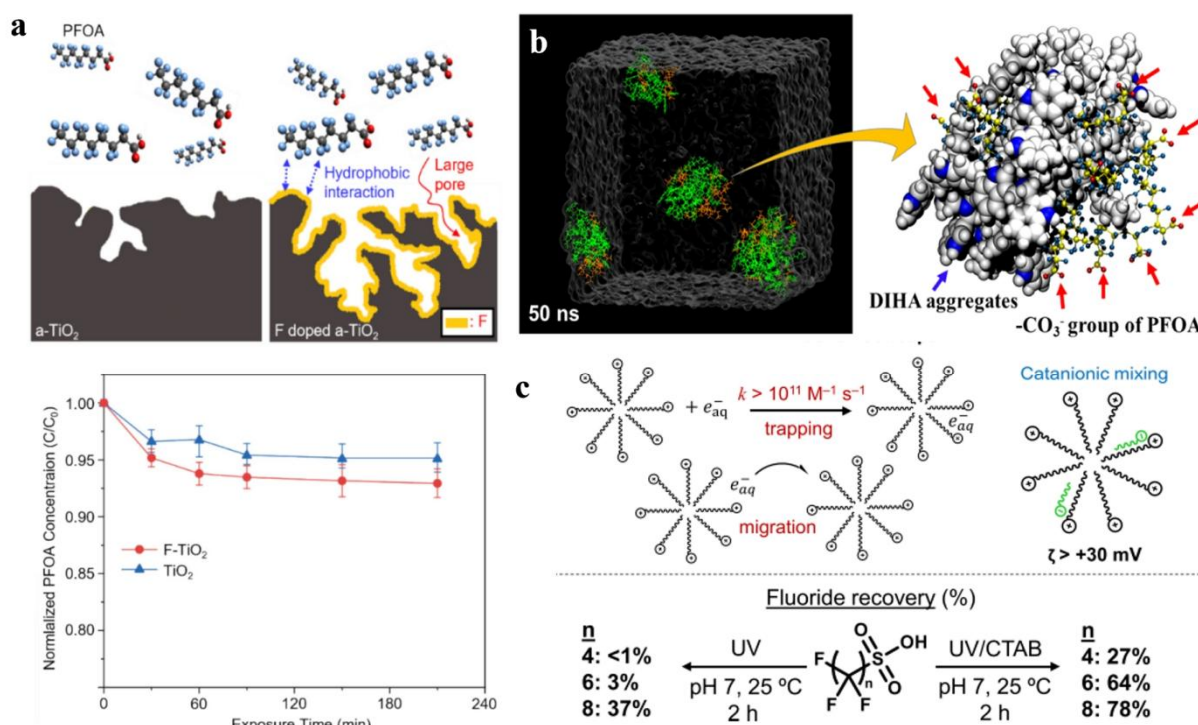


Figure 7. (a) Schematic of HF-induced surface etching (larger accessible area) and F-mediated hydrophobic interactions enhancing PFOA concentration [80]. (b) Molecular dynamic simulation of PFOA anions adsorbed onto the DIHA/DIHA⁺ nanospheres after running for 50 ns, and adsorption model of PFOA on the DIHA aggregate. Adapted with permission from Ref. [108]. Copyright © 2023 American Chemical Society (c) Trapping of e_{aq}^- by cationic micelles and surface charge for catanionic micelles and fluoride recovery from PFSA destruction. Adapted with permission from Ref. [79]. Copyright © 2025 American Chemical Society.

Cationic CTAB micelles can serve as nanoconfinement platforms that trap e_{aq}^- and deliver them to PFAS, dramatically enhancing defluorination efficiency by shifting the bottleneck from e_{aq}^- abundance to utilization. Fan et al. [79] constructed CTAB/PFAS catanionic micelles. (Figure 7c) that capture e_{aq}^- generated directly from water photolysis. Without any external photosensitizer, this nanoconfinement achieves near-complete defluorination of diverse PFAS, including short-chain PFBS (fluoride recovery ~100%), by suppressing electron recombination and protecting e_{aq}^- from oxygen scavenging. Similarly,

Eom et al. [109] built CTAB/GenX micelles, which enables efficient GenX degradation at neutral pH under air, achieving 86% removal and 40% defluorination within 6 h.

4.3. Light Absorption Engineering

The solar spectrum consists of only ~3–5% UV light, yet many benchmark photocatalysts (TiO_2 , Ga_2O_3 , In_2O_3) require UV excitation due to their wide bandgaps (>3.0 eV). Expanding light absorption into the visible and near-infrared regions is therefore essential for energy-efficient, solar-driven PFAS defluorination.

4.3.1. Narrow-Bandgap Semiconductor Engineering

Narrow-bandgap semiconductors can absorb visible light directly, reducing the reliance on UV irradiation and enabling operation under sunlight or low-energy LED sources. For instance, hexagonal ZnIn_2S_4 (ZIS) nanosheets [110], with a bandgap of approximately 2.36 eV, were demonstrated superior photocatalytic activity for PFAS degradation under both simulated sunlight and visible-light irradiation ($\lambda > 420$ nm). More than 99% of sodium OBS was degraded within 1.5 h of visible-light irradiation ($k = 0.063 \text{ min}^{-1}$), substantially outperforming P25 TiO_2 , which achieved only 12% degradation under identical conditions due to its negligible visible-light response. The enhanced performance was attributed to enhanced light absorption and facilitated charge separation.

To extend the absorption edge of wide-bandgap photocatalysts into the visible region, elemental doping and solid-solution formation have been widely employed. Nitrogen doping of In_2O_3 reduced its bandgap from 2.78 eV to 2.61 eV, enabling complete PFOA degradation within 6 h under simulated sunlight [111]. Similarly, Br-doped BiOI ($\text{BiOI}_{0.95}\text{Br}_{0.05}$) solid solution tuned the band structure, increasing the PFOA degradation rate constant by a factor of 4.3 compared with pristine BiOI, though detailed defluorination data remain limited [112]. Doping engineering has also been successfully extended to low-toxicity Cu-doped ZnS nanocrystals, which exhibit extended optical absorption into the visible region, enabling visible-light-driven PFOS defluorination that is otherwise unattainable with undoped ZnS [113]. Beyond single-component doping, heterojunction construction offers an additional strategy: coupling narrow-bandgap sulfides with bismuth oxyhalides extends light absorption while preserving the favorable oxidation potential of the wide-bandgap component. $\text{CuInS}_2/\text{BiOCl}$ composites, for example, achieve approximately 60% PFOA defluorination under simulated sunlight [84], demonstrating the feasibility of solar-driven PFAS treatment.

The trade-off inherent in narrow-bandgap engineering is that reduced bandgap typically lowers the conduction band minimum, diminishing the reduction potential of photogenerated electrons. For PFAS defluorination, which requires highly reducing species to cleave C–F bonds, excessively narrow bandgaps may be counterproductive.

4.3.2. Plasmon Resonance Effect

Plasmonic nanoparticles exhibit localized surface plasmon resonance (LSPR), concentrating electromagnetic fields at the nanoparticle surface and generating hot electrons that can be injected into adjacent semiconductors. This mechanism extends effective light absorption into the visible region while preserving the semiconductor's band structure and redox potentials. Bi nanoparticles integrated into $\text{BiOI}_{0.8}\text{F}_{0.2}$ solid solutions exhibited surface plasmon resonance effects, narrowing the bandgap and enhancing separation of photoinduced charge pairs, leading to complete PFOA degradation within 2 h under simulated solar light with a rate constant nearly 10 times that of pristine BiOI [114]. Additionally, Bhardwaj et al. [115] investigated the size-dependent plasmon dynamics and direct hot electron transfer (DHET) from Ag nanoclusters (Ag_{13} to Ag_{309}) to PFOA and PFOS based on real-time time-dependent density functional theory. DHET probability decreases from ~50% (Ag_{13}) to ~2% (Ag_{309}), but net electron transfer is controlled by electronic structure matching. Larger clusters (Ag_{147} , Ag_{309}) enable stable unidirectional charge transfer, while smaller ones show reversible Rabi oscillations.

4.4. Macrostructural Design and Synergy Systems

Laboratory-scale photocatalysis studies often employ suspended nanoparticles with high surface-area-to-volume ratios, achieving impressive defluorination efficiencies under idealized conditions. However, translating these results to field applications requires addressing catalyst recovery, long-term stability, continuous-flow operation, and performance in complex water matrices that contain dissolved ions, natural organic matter, and co-contaminants.

4.4.1. Macrostructural Catalyst Engineering

MOF-based porous nanostructures offer high surface areas and abundant active sites while maintaining structural integrity under photocatalytic conditions. The titanium-based MOF MIL-125-NH₂ achieved over 98.9% PFOA degradation within 24 h under Hg-lamp irradiation [116], demonstrating the potential of MOF architectures for PFAS photodegradation.

Immobilization of photocatalysts on macroscopic supports—membranes, foams, sponges, or magnetic particles—addresses the critical recovery challenge that has hindered the practical application of nanoparticle-based photocatalysts. An iron-enhanced titanium nanotube activated carbon composite coating on ultrafiltration membranes was investigated in a photo-membrane reactor (PMR) under UV irradiation. The membranes removed up to 80% of the initial PFOA within 2 h, with an average removal of 69% over two 8-h operation cycles. When tested on a mixed PFAS solution, PFOA removal decreased to 35%, but 46% of PFOS was still removed, and notably, 95% of the adsorbed PFOA was destroyed [117].

Matthews et al. [118] designed a continuous flow photoreactor with customizable internal chamber volume. Multiple photocatalyst films were prepared by drop casting, and efficient photocatalytic degradation of dyes, a model fluorobenzoic acid, and PFOS was achieved under either single-pass or circulating flow modes. The system demonstrated catalyst film stability for over 8 days and integrated online ion and spectral detection.

4.4.2. Synergy Systems for Enhanced Defluorination Efficiency

Photoelectrocatalysis (PEC) combines photocatalysis with an applied bias to suppress electron–hole recombination and maintain high carrier utilization in complex water matrices. A TiO₂-based bias-enhanced photocatalytic (BEEP) system, using highly ordered nanoporous TiO₂, shows that a small bias not only reduces recombination and ionic interference but also increases efficiency under high salinity—attributed to prevented ion-induced recombination and possible generation of reactive chlorine species. The BEEP system performs effectively in both fresh and salt water [119]. Besides, a supercapacitor-assisted electrophotocatalytic system that integrates photochemical and electrochemical energy was developed [76]. The organic photoreductant KQGZ injects electrons into the inert C–F bonds of PTFE and other PFASs under visible light, while the supercapacitor serves as a portable and renewable electron source to generate catalytically active species without excess sacrificial donors. This hybrid system achieves up to 96% defluorination of PTFE under mild conditions and can be powered by sunlight, demonstrating a practical and energy-efficient platform for PFAS destruction. More recently, a Pd-decorated TiO₂ cathode enables efficient photoelectrochemical degradation of PFOS under ambient conditions. Operando spectroscopy and DFT calculations reveal that cathodic bias promotes PFOS adsorption on TiO₂, while UV-excited Pd sites generate hot electrons that directly cleave C–F bonds or form hydrated electrons for indirect reduction. This dual pathway achieves rapid, deep defluorination even in reverse osmosis concentrate and AFFF-impacted water. Scalable single-chamber reactors and mesh cathodes have been demonstrated [77].

4.5. Operating Conditions

While the preceding subsections have addressed catalyst-level design strategies—including electronic structure modulation, interface engineering, light absorption broadening, and macrostructural design—the final layer of optimization involves operational parameters that can be adjusted during system operation to maximize defluorination performance. These parameters, including light source characteristics, catalyst loading, initial PFAS concentration, and temperature, are distinct from the intrinsic factors discussed in Section 3 in that they are readily controllable and can be optimized empirically for a given catalyst–substrate system. The following subsections systematically discuss these adjustable parameters and their respective impacts on defluorination efficiency.

4.5.1. Light Wavelength and Intensity

The widespread use of 254 nm irradiation in photocatalytic PFAS studies derives primarily from the emission characteristics of low-pressure mercury lamps, which exhibit a strong spectral line at 253.7 nm with a wall-plug efficiency of approximately 30–40% and operational lifetimes of 8000–12,000 h. However, the notion that 254 nm light directly photolyzes PFAS warrants caution, as most perfluoroalkyl substances exhibit negligible molar absorptivity above ~220 nm—PFOA, for instance, has a decadic molar absorption coefficient of only ~3.5 M^{−1} cm^{−1} at 254 nm [120,121]—and the quantum yields for direct photolysis are

correspondingly low (on the order of 10^{-5} to 10^{-4} mol einstein $^{-1}$) [122]. When comparing photocatalytic activities across studies, quantitative optical metrics—including irradiance, photon flux, emission spectrum, and reactor geometry—are essential, as nominal lamp wattage ratings (e.g., 16 W vs. 32 W) do not reflect the photon dose actually delivered to the sample. Increasing light intensity generally accelerates defluorination up to a saturation point, beyond which further gains are limited by charge carrier recombination or mass transfer constraints. Visible light typically affords lower defluorination efficiencies owing to the limited photon energy available for activating wide-bandgap photocatalysts, yet it offers the practical advantage of compatibility with solar irradiation. The implementation of UVC and VUV systems is further constrained by several practical considerations: water absorbs 185 nm VUV radiation strongly, with a penetration depth of less than 1 cm, necessitating thin-film or annular reactor designs; conventional glass reactors are unsuitable and must be replaced with quartz or UV-transparent materials; the wall-plug efficiency of VUV generation remains low (~ 6 – 15%) [123]; and the finite lamp lifetimes impose additional operational and economic burdens.

4.5.2. Catalyst Dosage

An optimal catalyst dosage exists. At low dosage, insufficient active sites limit defluorination; at excessive dosage, light scattering and screening reduce photon absorption. For Fe/TNTs@AC, the best PFOA defluorination (62% in 4 h) was achieved at 1.0 g L^{-1} ; increasing to 2.0 g L^{-1} decreased defluorination to 48% due to aggregation and light attenuation [94].

4.5.3. Initial PFAS Concentration

Defluorination efficiency is typically higher at lower initial PFAS concentrations because the limited amounts of reactive species can attack each PFAS molecule more thoroughly. For In_2O_3 , decreasing the initial PFOA concentration from 100 mg L^{-1} to 10 mg L^{-1} increased the defluorination efficiency from 33% to 71% after 4 h [100]. However, at extremely low concentrations ($\mu\text{g L}^{-1}$ range), mass transfer limitations may slow down the reaction kinetics.

4.5.4. Temperature

Elevated temperature generally accelerates defluorination by increasing molecular collision frequency and facilitating charge carrier mobility. In a heat-activated persulfate system, raising the temperature from 20 to 70 °C increased the defluorination rate constant of PFOA from 0.0012 h^{-1} to 0.0915 h^{-1} [124]. However, too high temperatures ($> 80\text{ °C}$) may lead to catalyst deactivation or unwanted side reactions.

5. Conclusions and Outlook

5.1. Conclusions

In summary, this review establishes a defluorination-oriented framework that moves beyond degradation-centric thinking. By clarifying the distinct roles of reactive species, comparing the defluorination efficiency and intermediate toxicity of major pathways, and synthesizing integrated design strategies, it provides a mechanistic roadmap for the rational development of next-generation photocatalytic PFAS defluorination technologies. Reductive species are identified as the primary drivers of C–F bond cleavage, whereas oxidative species play auxiliary roles in headgroup activation. Among major pathways, the DHEH mechanism and redox-synergistic systems achieve near-complete defluorination, while H/F exchange often stalls at toxic, partially fluorinated intermediates. Defluorination efficiency is governed by PFAS molecular structure, solution pH, water matrix, and operating conditions. Based on these, four integrated design strategies are synthesized: electronic structure modulation; interface chemistry engineering; light absorption broadening; and macrostructural hybrid systems. The insights presented here aim to guide researchers toward systems that not only remove PFAS from water but truly destroy them—cleaving C–F bonds to achieve complete detoxification.

5.2. Outlook

While significant progress has been made, the path toward a sustainable and efficient photocatalytic PFAS remediation technology requires concerted efforts to address the following future research directions:

(1) To bridge the mineralization gap and achieve complete defluorination, future research must advance both mechanistic understanding and catalyst design. Regarding deep mechanistic understanding, investigations should go beyond degradation pathways to elucidate the kinetic and thermodynamic barriers that halt defluorination at short-chain intermediates. Advanced in situ characterization techniques, such as time-resolved spectroscopy and operando Raman, should be integrated with sophisticated computational methods, including *ab initio* molecular dynamics and machine learning potential-based density functional theory, to map the complete reaction coordinate from parent PFAS to CO_2 and F^- . In terms of designing for deep defluorination, catalyst design should shift from merely enhancing initial degradation to promoting complete defluorination. This requires creating surface sites with high affinity for short-chain PFAS and sufficient redox potential to cleave their C–F bonds. Furthermore, tandem systems—such as oxidative pretreatment followed by reductive polishing, or the reverse sequence—should be systematically optimized to achieve near-quantitative defluorination of complex PFAS mixtures.

(2) To achieve rational and data-driven catalyst discovery, the vast chemical space of photocatalyst compositions—such as multi-metal metal–organic frameworks, high-entropy oxides, and doped carbon nitrides—must be addressed, which necessitates high-throughput experimental and computational screening. Integrating machine learning with density functional theory calculations can accelerate the identification of promising candidates by predicting band edge positions, PFAS adsorption energies, and catalyst stability based on elemental composition and structural features. Furthermore, future catalysts should be designed with distinct and cooperative functional sites: for example, one site optimized for PFAS adsorption via fluorophilic or hydrophobic interactions, a second site responsible for efficient light absorption and charge separation, and a third site (e.g., single-atom metal) dedicated to lowering the activation energy of C–F bond cleavage. The interfaces between these functional domains are where synergy is maximized.

(3) In system-level design for real-world complexity, overcoming the inhibitory effects of dissolved organic matter requires research efforts to focus on engineering catalyst surfaces that are selectively permeable to PFAS. This can be achieved by creating a fluorophilic shield on the catalyst surface or by employing pre-concentration/separation steps, such as coupling with ion exchange or nanofiltration. The development of robust and fouling-resistant photocatalytic membrane reactors represents a key solution. Meanwhile, the “capture-and-destroy” strategy must be validated at pilot scale, which necessitates the design of durable, macrostructured adsorptive photocatalytic materials (e.g., floating spheres, packed beads, or monolithic aerogels) that can be readily recovered and regenerated. The integration of photocatalysis with real-time PFAS sensors for intelligent, on-demand treatment remains a long-term goal.

(4) In terms of environmental sustainability assessment, the development of stable and highly active visible-light photocatalysts is paramount for the economic viability of photocatalytic defluorination strategies. Research should prioritize natural sunlight as the energy source and evaluate defluorination performance under diurnal cycles and varying weather conditions, moving away from energy-intensive artificial UV sources. Furthermore, a standardized sustainability evaluation framework should be established, including energy efficiency analysis based on Electrical Energy per Order, life-cycle carbon footprint accounting of the catalysts, and techno-economic comparisons with existing treatment technologies such as granular activated carbon and ion exchange. Only by integrating laboratory efficiency with real-world energy consumption, cost, and environmental impact can photocatalytic defluorination technologies be advanced toward practical applications.

Author Contributions

J.H.: Writing, original draft preparation, and visualization; C.W. and H.W.: investigation, data curation, visualization; W.G. and Z.L.: investigation, visualization; Q.Z. and Y.G.: review and editing; Y.Z.: Supervision, review, and editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

The data are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflict of interest. Given the role as Editor-in-Chief, Yongfa Zhu had no involvement in the peer review of this paper and had no access to information regarding its peer-review process. Full responsibility for the editorial process of this paper was delegated to another editor of the journal.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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