

Cite this: *Mater. Adv.*, 2026,
7, 3101

Multifaceted advances in TiO₂-based photocatalysts for PFAS degradation: a critical review of mechanisms, modifications, and challenges

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The global persistence of per- and polyfluoroalkyl substances (PFAS), often referred to as “forever chemicals,” poses significant environmental and human health risks, driving regulatory action and intensified research into effective remediation strategies. Photocatalysis has emerged as a promising, sustainable approach for PFAS degradation via light-driven redox processes. Titanium dioxide (TiO₂) remains the benchmark photocatalyst due to its chemical stability, low toxicity, and strong oxidative potential; however, its practical application is limited by rapid electron–hole recombination, restricted visible-light absorption, and pH-dependent surface charge behavior, necessitating acidic conditions for optimal performance. These constraints reduce its efficacy against the robust carbon–fluorine bonds characteristic of PFAS and complicate large-scale deployment. Recent advances focus on multifunctional TiO₂-based systems, including metal and nonmetal doped systems, carbonaceous composites, heterojunctions, molecularly imprinted polymers, and adsorptive concentrate-and-destroy supports. Integration with advanced oxidation and reactor-level engineering approaches, such as photoelectrocatalysis (*i.e.*, photocatalysis under applied bias) and hybrid oxidants, has further advanced photocatalytic degradation technology under broader operating conditions. This review provides a critical comparative assessment of these strategies, highlighting mechanistic insights, structure–activity relationships, and practical limitations related to pH, stability, and scalability. By consolidating recent innovations and operational considerations, this work offers guidance for the rational design of efficient, field-relevant, and sustainable photocatalytic technologies for global PFAS remediation.

Received 29th October 2025,
Accepted 9th January 2026

DOI: 10.1039/d5ma01247c

rsc.li/materials-advances

1. Introduction

Scientific and technological progress has transformed modern society, improving healthcare, sanitation, transportation, and daily life. Central to these advances, materials science has enabled breakthroughs, from polymers to semiconductors and nanomaterials, elevating global living standards. However, history highlights the unintended environmental consequences of innovation, exemplified by chlorofluorocarbons (CFCs), asbestos, dichlorodiphenyltrichloroethane (DDT), and plastics.^{1–4} Today, per- and polyfluoroalkyl substances (PFAS) represent a pressing concern. Often termed “forever chemicals,” PFAS are characterized by strong C–F bonds, high chemical stability, bioaccumulation potential, and extreme environmental persistence.^{5–8} First synthesized in the late 1930s and commercialized by the 1940s,⁹ PFAS have been extensively applied in Teflon™

coatings, Scotchgard™ treatments, aqueous film-forming foams (AFFFs), textiles, semiconductor manufacturing, food packaging, and aerospace industries.^{9,10} United States (US) annual production of basic fluoropolymers reached 85 000 tons in 2018, forming the start of the PFAS value chain^{10,11} and contributing to widespread contamination of industrial zones, remote ecosystems, Arctic wildlife, and human blood samples worldwide.¹² Their persistence, mobility, and toxicity now pose severe environmental and public health challenges.¹³

Diverse remediation strategies have been explored for PFAS contamination, including adsorption (activated carbon, ion-exchange resins, MOFs, and engineered clays);^{14–20} advanced oxidation processes (AOPs) such as Fenton chemistry, persulfate activation, and electrochemical oxidation;^{21–23} photocatalysis;²⁴ thermal methods (incineration and supercritical water oxidation);^{24–26} biological approaches with PFAS-tolerant microbial consortia;^{27–29} plasma-based treatments;^{30,31} membrane separation (nanofiltration and reverse osmosis);^{32,33} and hybrid strategies integrating ultrasound, photolysis, or catalysis.^{34–36} Among these, photocatalysis has gained attention as a sustainable,

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environmentally benign approach. By harnessing sunlight or artificial UV light, photocatalysis generates reactive oxygen species (ROS) capable of cleaving robust C–F bonds.^{24,37–39} While numerous new strategies and materials are being explored in this field, a few recent examples of advancements include carbazole-cored super-photoreductants for low-temperature PFAS and PTFE defluorination,⁴⁰ CdIn₂S₄ micro-pyramids,⁴¹ Fe/g-C hybrids,⁴² rGO/WO₃ nanoflowers,⁴³ and Pb-doped TiO₂/rGO composites,⁴⁴ many achieving near-complete PFAS degradation through synergistic redox and radical-mediated pathways.

Within this context, TiO₂ remains at the core of photocatalysis, alone and in hybrid systems, owing to its high stability, low toxicity, cost-effectiveness, and strong oxidative potential under UV irradiation.^{45–49} The d⁰ electronic configuration of Ti⁴⁺ results in Ti 3d-O 2p hybridization, producing a ~3.0–3.2 eV bandgap suitable for UV-driven photocatalysis. Upon excitation, TiO₂ generates electron–hole (e[−]–h⁺) pairs that drive ROS formation, particularly •OH and O₂•[−], which are central to pollutant degradation.^{50,51} Photocatalytic performance is strongly influenced by crystal polymorphs (anatase, rutile, and brookite), lattice structure, and facet-specific reactivity. For example, anatase {001} facets (surface energy ~0.90 J m^{−2}) exhibit a higher reactivity than {101} facets (~0.44 J m^{−2}).^{52–54} A representative strategy involves selective Pt single-atom deposition on facet-engineered TiO₂, stabilization of {001} facets using fluoride ions, APTMS (amino-propyltrimethoxysilane) anchoring to guide Pt precursors to {101}, and mild UV irradiation to reduce Pt to single atoms. This spatially separates oxidative and reductive sites; holes migrate to {001} for •OH generation, while Pt atoms on {101} trap electrons for reductive defluorination, enabling simultaneous oxidative–reductive PFAS degradation. Surface chemistry further modulates TiO₂ activity, with hydroxyl groups, coordinatively unsaturated Ti sites, oxygen vacancies, and Ti³⁺ centers serving as active sites for adsorption, charge separation, and visible-light absorption.^{55–60} Controlled defect introduction *via* hydrogenation, electrochemical reduction, ion-thermal processing, ultrasonication, NaBH₄ treatment, microwave irradiation, plasma, or laser ablation enhances photocatalytic efficiency by suppressing e[−]–h⁺ recombination and extending optical response. Additional strategies include metal and nonmetal doping for bandgap tuning, heterojunction construction and fabrication of plasmonic–carbonaceous composites for charge separation, co-catalyst loading to enhance e[−]–h⁺ utilization, surface functionalization to promote pollutant adsorption, modulation of reactive species for optimized ROS balance, fabrication of hierarchical nanostructures, and formation of mixed anatase–rutile interfaces that facilitate charge migration.^{61–65} Hydrophilic or fluorophilic surface tailoring has been shown to enhance interactions with polar and fluorinated substrates.^{66,67} Synergistic integration of TiO₂ photocatalysis with electrochemical,⁶⁸ photo-Fenton,⁶⁹ or piezocatalytic⁷⁰ processes generates additional radical pathways, while immobilization in thin films and porous monoliths improves scalability. TiO₂-based photocatalytic systems, owing to their intrinsic stability, structural tunability, and broad adaptability, continue to serve as a cornerstone for ROS-mediated pollutants degradation. Fig. 1 shows key strategies

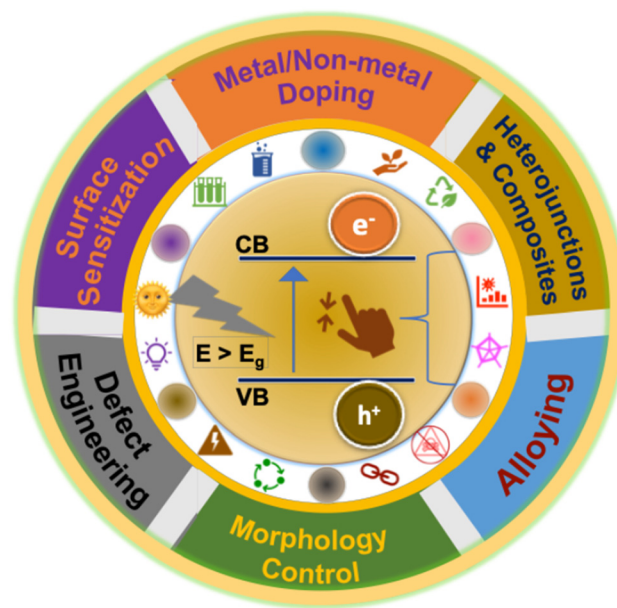


Fig. 1 Key strategies for enhancing photocatalysts' performance in environmental remediation to improve light absorption, charge separation, and pollutant degradation, enabling next-generation, effective, and field-applicable solutions.

for enhancing photocatalysts' performance in environmental remediation.

This review presents a comprehensive evaluation of TiO₂-based photocatalysts for PFAS degradation, covering pristine and modified materials, including defect-engineered, single-atom, carbonaceous, heterojunction, and adsorptive designs. It critically examines operational parameters, mechanistic pathways, and structural modifications that govern adsorption, charge separation, reactive species generation, and oxidative–reductive defluorination. Hybrid and integrated strategies, such as photoelectrocatalysis, advanced oxidation, and reactor-level innovations, are discussed to address inherent limitations like charge recombination, UV dependence, and mass-transfer constraints. By connecting mechanistic insights with practical considerations, including stability, recyclability, matrix effects, energy efficiency, and scalability, this review provides guiding principles for designing next-generation TiO₂-based photocatalysts that are efficient, robust, and field-relevant for sustainable PFAS remediation.

2. Chemical, environmental, and health context of PFAS

Per- and polyfluoroalkyl substances (PFAS) are a global environmental concern due to their chemical stability, persistence, and widespread application. PFAS originated in 1938 when Dr Roy J. Plunkett at DuPont accidentally synthesized polytetrafluoroethylene (PTFE) while developing chlorofluorocarbon refrigerants.^{71,72} Commercialized as Teflon™ in 1948, PTFE's robust C–F bonds confer thermal and chemical stability, catalyzing thousands of



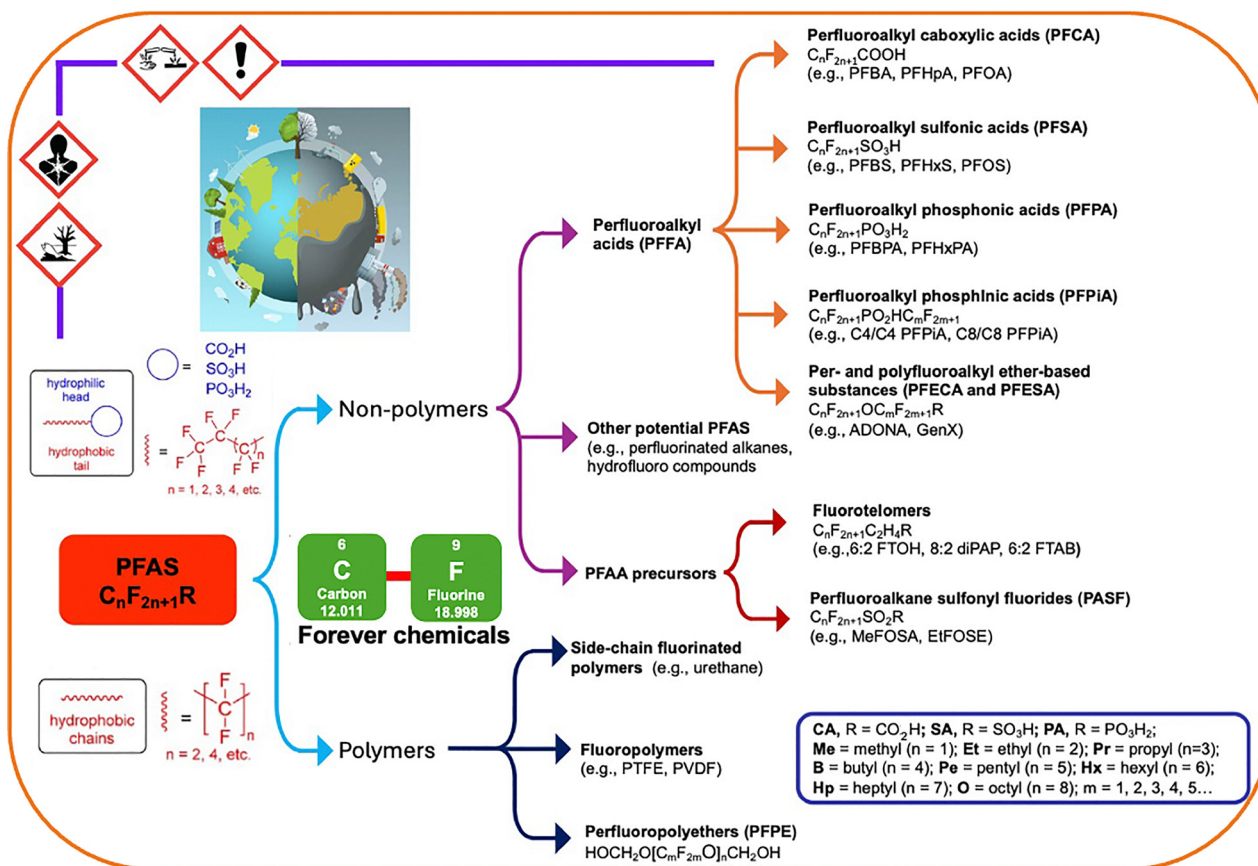


Fig. 2 Classification of PFAS based on structural features: categorized into polymeric and non-polymeric groups, redraw from ref. 81. A few parts of this figure are adapted from open-source graphical elements available on Freepik (<https://www.freepik.com>), designed by macrovector/Freepik.

PFAS compounds used in firefighting foams, surfactants, textiles, microelectronics, and other applications.^{73,74} These properties also make PFAS “forever chemicals,” leading to persistence and bioaccumulation in soil, water, air, and biota.^{75–78} Despite phase-outs of legacy PFAS such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), new analogues continue to be produced with similar mobility and toxicity.⁷⁹ PFAS comprise over 14 000 compounds, broadly classified as non-polymeric or polymeric (Fig. 2).^{80,81} Non-polymeric PFAS contain a hydrophobic perfluoroalkyl chain ($-C_nF_{2n}-$) linked to polar groups (carboxylate and sulfonate), enabling surfactant applications like aqueous film-forming foams (AFFFs), metal plating, and cleaning agents.⁸² Polymeric PFAS, including PTFE and FEP (fluorinated ethylene propylene), are high-molecular-weight fluoropolymers used in cookware, electronics, and waterproof fabrics. The chain length and functional groups influence mobility, bioaccumulation, and degradability: short-chain PFAS are highly mobile yet hard to remove, whereas long-chain PFAS readily bioaccumulate.^{83,84} Emerging variants with unknown fate challenge regulatory and analytical frameworks, prompting tools like PFAS-Atlas for chemical mapping and prioritization.^{85,86}

PFAS are detected in surface water, groundwater, drinking water, soils, vegetation, and biota worldwide, including remote Arctic and Antarctic regions.^{87–91} HRMS and LC-MS/MS detect PFAS at parts-per-trillion levels, revealing widespread contamination and bioaccumulation.^{92–94} Human exposure occurs *via*

ingestion, inhalation, and dermal contact.^{95–97} Epidemiological studies, the C8 Health Project (> 69 000 individuals), link chronic PFOA exposure to testicular and kidney cancers, thyroid disorders, ulcerative colitis, and pregnancy-induced hypertension.^{98,99} PFAS interact with nuclear receptors (PPAR α , CAR, and PXR), perturb lipid metabolism, immunity, and hormonal regulation, and cross the placental barrier.^{100–102} Blood levels correlate with diet, smoking, and use of PFAS-containing products.^{103,104}

Ecologically, PFAS induce biochemical disturbances at environmental concentrations. Metabolomic studies reveal altered gene expression in zebrafish larvae, liver glycogen depletion, and shifts in earthworm metabolites,^{105–107} rodent studies report neurological and metabolic effects at low doses.^{108,109} Risk assessments indicate low-to-moderate global risk, though industrial discharges can elevate exposure.^{110–112} AFFFs remain a major source, with contamination documented at military, industrial, and civilian sites.^{112–120} Research now focuses on fluorine-free alternatives, supported by United States Department of Defence (DoD), Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) initiatives.^{120,121} In parallel, international regulations are also emerging: most Australian states restrict PFAS foams for non-aviation use,^{122,123} and in 2023, five European Union (EU) member states proposed banning all PFAS in firefighting foams.¹²⁴ These exemptions highlight the need to integrate material innovation, regulation, and deployment to mitigate legacy and future PFAS exposure.

3. Prospective approaches to PFAS elimination

PFAS contamination in aqueous and soil matrices presents distinct remediation challenges. Water treatment strategies include adsorption, membrane filtration, and advanced oxidative or reductive methods, such as photocatalysis, electrochemical oxidation, electron beam irradiation, and hydrothermal alkaline treatment.^{125–127} While adsorption and membrane separation effectively concentrate PFAS, they often generate secondary waste requiring destructive post-treatment.¹²⁵ Advanced oxidative and reductive processes target mineralization but typically demand high energy, specialized catalysts, or extreme conditions, limiting large-scale applicability. Hybrid treatment trains that combine selective concentration with destructive pathways improve degradation efficiency while mitigating cost and secondary pollution.¹²⁵ However, complex aqueous matrices containing competing ions or natural organic matter can inhibit reactive species, underscoring the need for site-specific optimization.¹²⁸ As summarized in Fig. 3, PFAS treatment technologies include both destructive methods, such as photocatalysis, electrochemical oxidation, and hydrothermal or mechanochemical degradation, and non-destructive approaches, including adsorption, membrane filtration, and phytoremediation.¹²⁵ Hybrid systems that combine selective concentration with destructive pathways are also highlighted, illustrating strategies to enhance mineralization efficiency while minimizing secondary pollution.

Soil remediation faces additional hurdles due to heterogeneity and strong C–F bonds promoting PFAS retention.¹²⁹ Physical approaches, such as soil washing or amendment-induced immobilization, usually provide only temporary containment.^{130,131} Thermal strategies, including incineration and smoldering combustion

(> 500–900 °C), effectively destroy PFAS but require careful control of toxic fluorinated emissions.^{129,132–135} Energy-efficient smoldering of PFAS-laden granular activated carbon (GAC) and soils has achieved complete destruction, ~44% of PFAS on GAC and ~16% in soils, with emissions efficiently scrubbed by GAC.¹³⁶ Hydrothermal and supercritical water oxidation under alkaline conditions can remove >95% of PFAS, though effluent management remains critical.¹³⁷ Mechanochemical degradation using high-energy ball milling with additives (KOH and persulfate) provides non-thermal, onsite alternatives.^{138,139} Advanced oxidative and reductive methods, including electron beam irradiation and use of persulfate-based systems, generate radicals capable of cleaving C–F bonds but face high energy demands and matrix interference.^{125,138} Electrochemical remediation shows promise, particularly for short-chain PFAS, while phytoremediation offers a low-cost, sustainable option by sequestering PFAS in biomass for subsequent treatment.^{140–147}

Artificial intelligence (AI) and machine learning (ML) offer transformative potential for catalyst design and process optimization. By analyzing large PFAS datasets and reaction pathways, ML can predict outcomes and guide selection of optimal materials and operational conditions.^{148–151} Hybrid systems combining photocatalysis with electrochemical or mechanochemical processes exploit synergistic effects, enhancing mineralization efficiency and reducing by-product formation. Circular economy strategies, such as mechanochemical defluorination recovering fluorine as reusable salts, further enable sustainable PFAS waste management.¹⁵²

Among destructive methods, photocatalysis is particularly attractive, as it harnesses solar energy under ambient conditions to generate reactive oxygen species capable of mineralizing PFAS into environmentally benign products. Catalyst design approaches, including size-exclusion, charge heterogeneity, amphiphilic surface

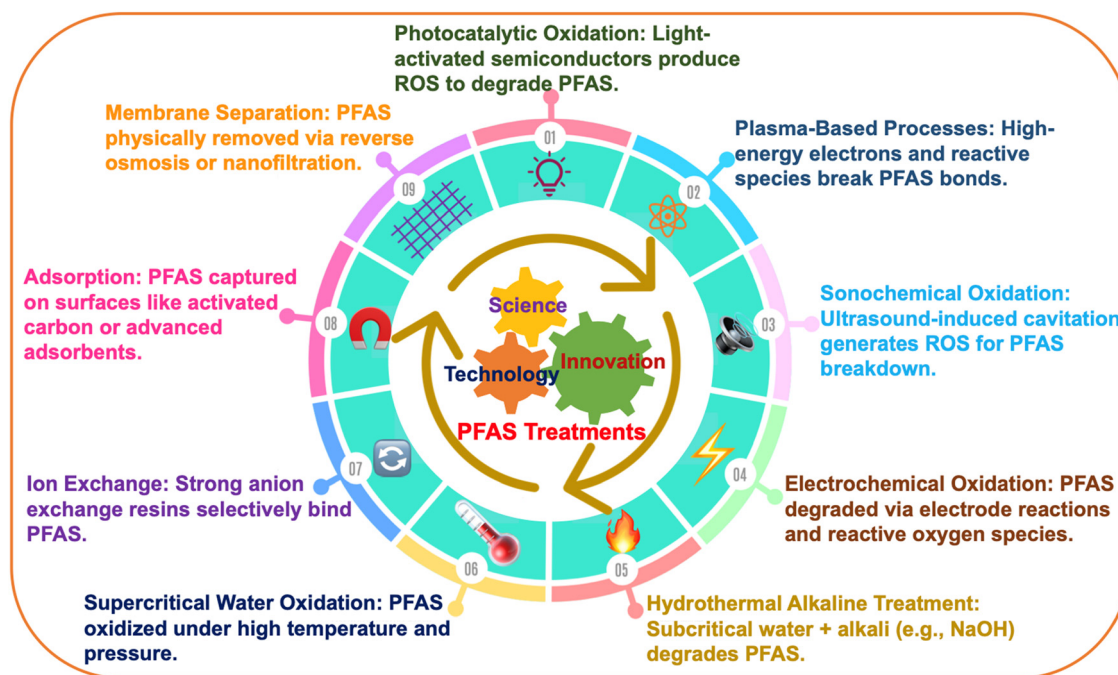


Fig. 3 Overview of destructive and non-destructive technologies for PFAS treatment, highlighting conventional approaches and advanced degradation strategies. Note: a few parts of this figure are adapted from open sources like Freepik (<https://www.freepik.com/>) and Pixabay (<https://pixabay.com/>).



modification, and molecular imprinting, enhance PFAS adsorption and orientation, improving degradation even in complex matrices.^{153–155} TiO₂-based photocatalysts are especially prominent due to their intrinsic tunability and versatility, allowing strategies such as facet engineering, doping, and heterojunction construction to create structurally and functionally diverse photocatalysts. This multifaceted platform underpins the focus of this review on strategies to enhance photocatalytic efficiency and selectivity for PFAS degradation.

4. Mechanistic foundations and limitations of TiO₂

Titanium dioxide (TiO₂) is widely recognized as a benchmark photocatalyst due to its strong oxidation potential, chemical

stability, and cost-effectiveness.¹⁵⁶ Upon absorption of photons with energy equal to or greater than its band gap (~ 3.2 eV for anatase), electrons are excited from the valence band to the conduction band, generating e^-h^+ pairs. Valence-band holes (h^+) serve as potent oxidants, while conduction-band e^- participate in interfacial reduction reactions, including oxygen reduction, leading to secondary reactive species under aerobic conditions^{3,157–159} (Fig. 4a). The overall photocatalytic efficiency is governed by the quantity of photo-generated charge carriers, their oxidation–reduction potentials, and charge-carrier recombination dynamics.

Per- and polyfluoroalkyl substances (PFAS), particularly perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFSAs), possess exceptionally strong carbon–fluorine (C–F) bonds,¹⁶⁰ which underpin their environmental persistence and resistance to conventional radical-mediated oxidation.¹²⁵ For representative

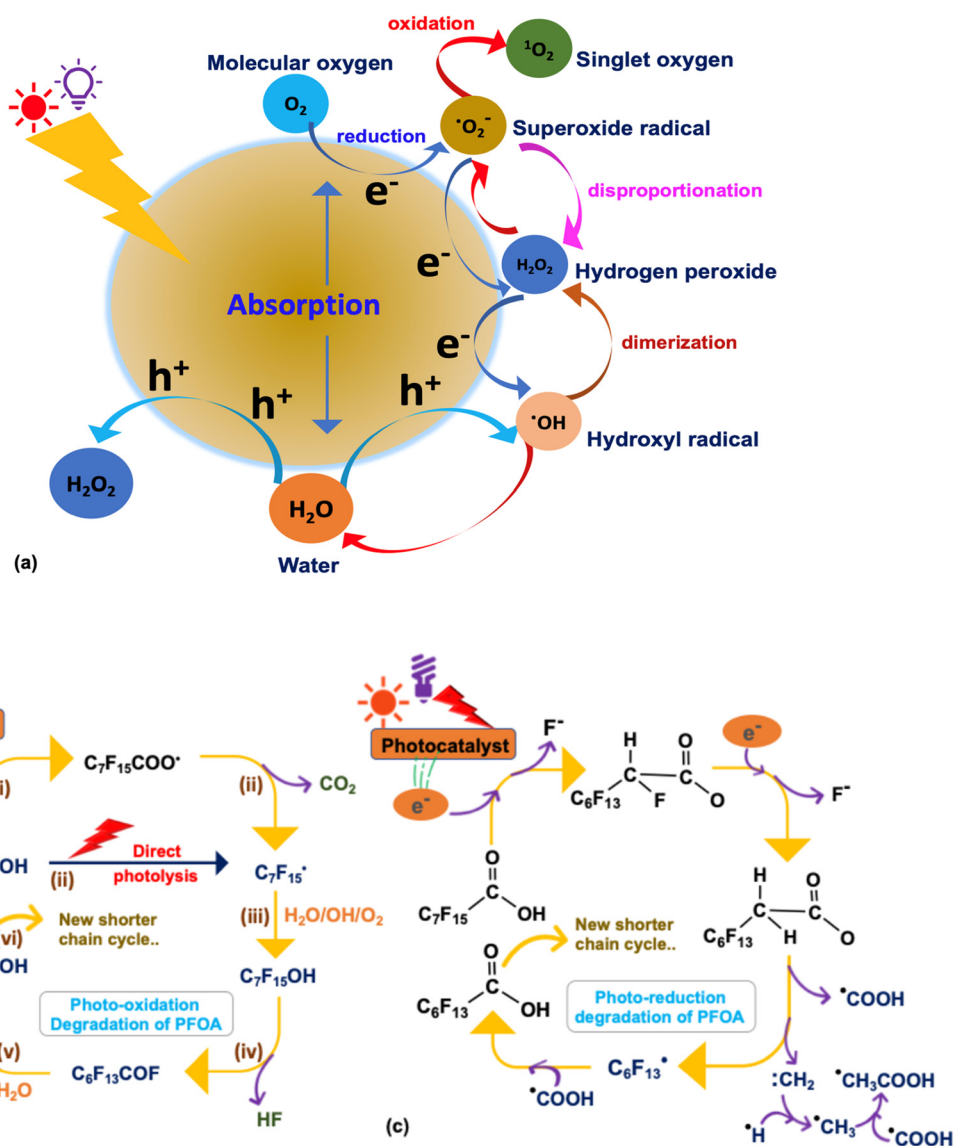


Fig. 4 (a) General photocatalytic mechanism depicting electron–hole pair formation and subsequent redox reactions; (b) general pathway of photo-oxidative degradation of PFOA; (c) typical pathway of photo-reductive degradation of PFOA.



compounds such as PFOA and PFOS, the fully fluorinated alkyl chains lack abstractable hydrogen atoms, rendering hydroxyl radical ($\bullet\text{OH}$) attack largely ineffective for initiating degradation.¹⁶¹ As a result, indirect oxidation pathways involving $\bullet\text{OH}$ contribute minimally to PFAS transformation, and reaction initiation is increasingly attributed to direct interfacial electron transfer between the pollutant and the photoexcited semiconductor *via* valence-band (VB) holes.^{161–163} For PFCAs, adsorption onto TiO_2 surfaces facilitates direct VB hole oxidation, triggering Kolbe-type decarboxylation of the head group (Fig. 4b) and generating carbon-centered radicals that undergo stepwise chain shortening to progressively shorter PFCAs (*e.g.*, PFHpA, PFHxA, PFPeA, PFBA, and PFPrA), accompanied by the formation of CO_2 and fluoride ions.^{125,162,163} These transformations are surface-controlled, making adsorption affinity and interfacial charge-transfer efficiency the primary determinants of degradation kinetics. Although photoexcited electrons react readily with dissolved oxygen to form superoxide radicals ($\bullet\text{O}_2^-$), this species is widely regarded as ineffective for PFAS degradation, and its role remains controversial.¹⁶² In oxygenated systems, electron scavenging by O_2 further suppresses reductive pathways by limiting the availability of excited electrons.¹⁶⁴

Complementary photoreductive pathways (Fig. 4c) have also been reported, particularly under anoxic conditions and in the presence of hole scavengers.^{161,162} In these systems, conduction-band electrons or hydrated electrons (e_{aq}^-) are injected into the PFAS molecule, leading to direct reductive cleavage of C–F bonds (Fig. 4c) or, in some cases, reductively induced decarboxylation of PFCAs.¹⁶⁵ However, such reductive mechanisms are strongly disfavored under environmentally relevant conditions due to efficient electron scavenging by oxygen and the generally low sorption affinity of semiconductors for PFAS.¹⁶⁶ While some studies report that $\bullet\text{O}_2^-$ scavengers hinder PFOA degradation, suggesting a possible role in initiating decarboxylation *via* nucleophilic substitution, others propose that $\bullet\text{O}_2^-$ may indirectly generate $\bullet\text{OH}$ under acidic conditions, thereby contributing to oxidative pathways.¹⁶² Consequently, the role of superoxide remains unresolved. Ateia *et al.*¹⁶³ proposed that PFAS degradation is primarily triggered by direct electron transfer to valence-band holes, with $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ playing a minimal role in initiating the reaction. In contrast, earlier studies conducted by Hori *et al.*¹⁶⁷ showed that the presence of moisture does not alter the primary degradation rate of fluorotelomer alcohols on TiO_2 , but does enhance the breakdown of fluorinated byproducts and the formation of CO_2 . This suggests that $\bullet\text{OH}$ radicals may be more important for the secondary oxidation and mineralization of intermediates rather than for the initial activation of PFAS molecules.

TiO_2 's intrinsic properties, including polymorphism, defect tolerance, electronic tunability, high dielectric constant, and chemical robustness, support diverse modification strategies. Its polymorphs (anatase, rutile, and brookite) can accommodate dopants, enabling band-gap modulation and the introduction of defect or mid-gap states that extend light absorption and influence charge-carrier dynamics. Facet engineering, particularly exposure of high-energy anatase $\{001\}$ facets ($\sim 0.90 \text{ J m}^{-2}$), provides selective adsorption and reaction sites that enhance

surface redox processes.¹⁶⁸ Surface features such as coordinatively unsaturated Ti sites, oxygen vacancies, and Ti^{3+} species improve charge separation, broaden optical absorption, and facilitate PFAS adsorption and interfacial electron transfer.^{169–171} Morphological flexibility, from nanoparticles to ordered mesoporous films, allows tuning of surface area, porosity, and light-harvesting efficiency, directly influencing adsorption, charge migration, and catalytic performance.^{172,173} Combined with chemical robustness under diverse aqueous conditions, TiO_2 remains durable for long-term photocatalytic applications.¹⁷⁴

Compared with alternative photocatalysts such as ZnO , $\text{g-C}_3\text{N}_4$, or CdS , which can suffer from photocorrosion, limited charge mobility, or toxicity, TiO_2 provides a balanced combination of stability, tunability, and cost-effectiveness.^{175,176} This multifaceted nature underpins rational design strategies, including doping, defect engineering, composite formation, and morphological control, that enhance PFAS degradation. The following sections focus on these intrinsic and engineered advances, highlighting their relevance for efficient PFAS mineralization under environmentally realistic conditions.

5. Pristine TiO_2 photocatalysis performance and challenges

Among TiO_2 polymorphs, anatase ($E_g \approx 3.2 \text{ eV}$) is the most widely employed for photocatalysis due to its more negative conduction band potential, slower e^- – h^+ recombination, and higher surface area compared to rutile ($\sim 3.0 \text{ eV}$) and brookite ($\sim 3.3 \text{ eV}$).^{177,178} Rutile offers superior thermal stability, and brookite remains underexplored due to synthetic challenges, while anatase generally exhibits higher photocatalytic activity for pollutant degradation under typical conditions, partly because its formation is kinetically favored at temperatures below $\sim 600 \text{ }^\circ\text{C}$, leading to smaller crystallite sizes and a higher density of active surface sites.^{179,180} TiO_2 synthesis *via* chemical (sol–gel, hydrothermal, and precipitation), physical (thermal oxidation and vapor deposition), or green/biological routes imparts control over size, crystallinity, morphology, and surface chemistry, which govern charge dynamics, reactive oxygen species (ROS) generation, and PFAS adsorption.^{181–184} Both commercial TiO_2 (*e.g.*, P25) and laboratory-tailored variants serve as references for mechanistic studies and catalyst development.

Foundational studies show that while TiO_2 efficiently mineralizes conventional organics, PFAS resist degradation due to strong C–F bonds and thermodynamically stable perfluoroalkyl backbones.^{185–187} Perfluorocarboxylic acid (PFCA) degradation typically follows a photo-Kolbe decarboxylation pathway, initiated at the terminal carboxyl group (Fig. 5a).¹⁸⁶ Solution pH is a critical factor influencing TiO_2 photocatalytic activity, as it affects surface charge, PFAS adsorption, aggregation, and reactive species generation.¹⁸⁷ The point of zero charge (pH_{pzc}) of TiO_2 is approximately 6.25. PFOA exists as an anion ($\text{C}_7\text{F}_{15}\text{COO}^-$) above its pK_a (2.8).¹⁸⁷ When pH ranges from 2.8 to 6.25, adsorption of $\text{C}_7\text{F}_{15}\text{COO}^-$ on the positively charged TiO_2 surface (Ti-OH_2^+) is enhanced by electrostatic interactions, facilitating oxidative degradation. Above pH 6.25, the



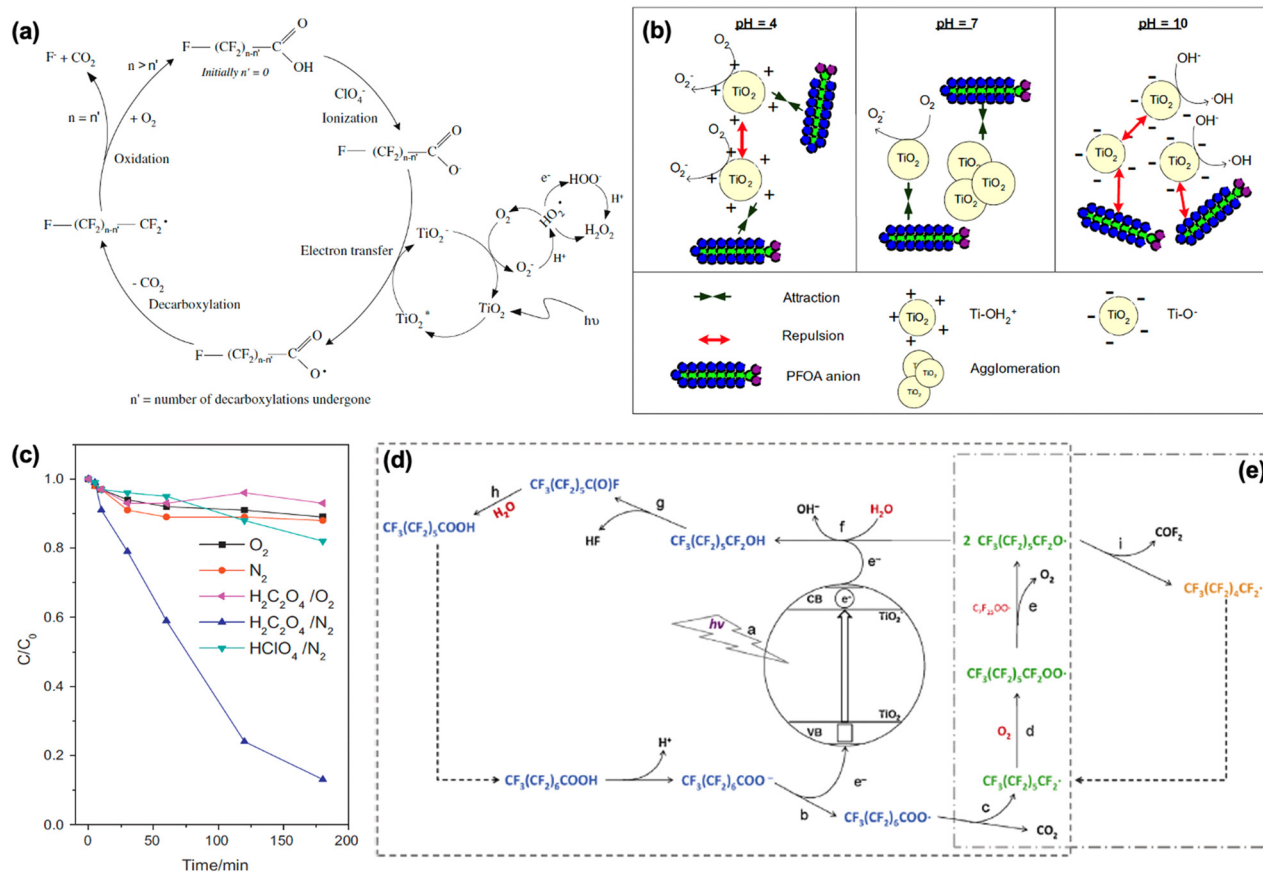


Fig. 5 (a) Proposed photocatalytic decomposition cycle of PFCAs on TiO₂ under UV light, involving ionization, electron transfer, decarboxylation, and oxidation. Successive CF₂-unit losses yield shorter-chain PFCAs until complete mineralization to CO₂ and F⁻ ions. Reproduced from ref. 186 with permission from Elsevier BV, copyright 2009; (b) schematic of TiO₂ surface charge effects on PFOA degradation across pH: Ti-OH₂⁺ dominates at acidic pH, Ti-OH at neutral (pH 6–7, zero-point charge), and Ti-O⁻ at basic pH. Despite expected higher degradation at low pH due to electrostatic attraction, experiments showed greater PFOA removal at basic pH (10), indicating that radical-driven processes outweigh surface charge effects. Reproduced from ref. 187 with permission from Elsevier BV, copyright 2009;¹⁸⁷ (c) photocatalytic degradation of PFOA by TiO₂ under 254 nm UV. Adsorption was <8%. After 180 min, removal reached 10.5% (O₂), 12.4% (N₂), 6.6% with oxalic acid (O₂), and 86.7% with oxalic acid (N₂). At pH 2.47 (HClO₄), only 17.8% removal occurred. Rate constants were 1.16 × 10⁻² min⁻¹ (oxalic acid) vs. 1.0 × 10⁻³ min⁻¹ (HClO₄). Defluorination was 16.5% with TiO₂/oxalic acid but <1% otherwise. Reproduced from ref. 188 with permission from Elsevier BV, copyright 2011; proposed reaction mechanism for PFOA degradation in the presence of a TiO₂ photocatalyst, incorporating both photo-redox (d) and β-scission (e) pathways. Reproduced from ref. 189 with permission from Elsevier BV, copyright 2015.¹⁸⁹

surface is negatively charged (Ti-O⁻), reducing adsorption and photocatalytic efficiency. Acidic conditions thus favor PFOA adsorption and degradation, whereas perfluorosulfonic acids (PFSAs) show limited reactivity, highlighting functional group-dependent degradability.¹⁸⁵ Panchangama *et al.* reported >99% decomposition of long-chain PFCAs (PFOA, PFNA, and PFDA) under acidic conditions, though overall mineralization reached only 38–54%.¹⁸⁶ Solution pH also influences the distribution and reactivity of key species. Acidic conditions favor heterogeneous ROS-driven oxidation, while alkaline conditions can enhance the formation of hydrated electrons (e_{aq}⁻) in homogeneous systems, supporting reductive mineralization pathways. High H₃O⁺ concentrations in acidic media can scavenge e_{aq}⁻, reducing reductive contributions, whereas alkaline conditions stabilize e_{aq}⁻, facilitating C-F bond cleavage and minimizing short-chain PFOA accumulation.¹⁶¹ Optimal TiO₂ loadings (~0.66 g L⁻¹) enabled complete PFOA removal

within 7 h; higher doses reduced efficiency due to light scattering and aggregation. Sonication-assisted TiO₂ photocatalysis under near-neutral conditions improved mass transfer, ROS formation, and dispersion, achieving 64% PFOA degradation over 8 h, with sol-gel TiO₂ outperforming P25.¹⁸⁷ Surface charge effects were decisive: below the point of zero charge (~pH 6–7), TiO₂ is positively charged, enhancing adsorption; above it, repulsion limits efficiency (Fig. 5b).

Reductive TiO₂ photocatalysis complements oxidative pathways for highly resistant PFAS. Conduction-band electrons, stabilized by hole scavengers (*e.g.*, oxalic acid), facilitate the formation of CO₂^{•-} radicals that promote stepwise C-F bond cleavage.^{188,190–192} Wang *et al.* achieved 86.7% PFOA degradation at pH 2.47 with oxalic acid (as a hole scavenger) *versus* 17.8% with perchloric acid (used to maintain the same pH but without providing hole-scavenging ability), with the pseudo-first-order rate constant $k = 1.16 \times 10^{-2} \text{ min}^{-1}$ (Fig. 5c), over



11 times higher than that under oxidative-only conditions.¹⁸⁸ Kinetic and mechanistic studies highlight two key PFAS degradation pathways under UV/O₂, a stepwise photo-redox route generating shorter-chain PFCAs and a direct β -scission pathway producing CO₂ and HF¹⁸⁹ (Fig. 5d and e). Fluoride accumulation on TiO₂ surfaces can passivate active sites, limiting mineralization (~32%) and fluoride release (~29%). Oxygen availability modulates pathway selectivity: varying atmospheres (air, O₂, and N₂) shifts the balance between photo-redox and β -scission.¹⁹³ Bio-synthesized TiO₂ nanoparticles offer sustainable alternatives. Plant extracts or microorganisms produce nanoscale TiO₂ with tunable size and morphology, enhancing PFAS adsorption and ROS generation.^{194–196} *Albizia lebbbeck*-derived TiO₂ achieved 95.6% PFOS degradation and 56.1% defluorination at pH 2 under UV-vis irradiation.¹⁹⁶ Smaller crystallites (8.8 nm at pH 12 vs. 12.1 nm at pH 8) improved charge separation and surface activity, illustrating the dual advantage of green synthesis: environmental benignity and enhanced photocatalytic efficacy. All the above studies indicated that pristine TiO₂ efficiently decomposes PFAS under optimized conditions, yet challenges including surface interactions,

catalyst passivation, functional group specificity, and reaction condition control constrain complete mineralization, highlighting the need for advanced material design and hybrid strategies.

Murgolo *et al.*¹⁹⁷ evaluated nanostructured TiO₂ films on stainless steel mesh and P25 TiO₂ (50–100 mg L⁻¹) for groundwater PFOS (200–400 μ g L⁻¹) under UV (254 nm, 60 min, pH 7.85), observing negligible degradation and highlighting the importance of reaction optimization. Furtado *et al.*¹⁹⁸ applied response surface methodology (RSM) to assess pH, catalyst dosage, and irradiation time. Acidic pH enhanced TiO₂ protonation and PFOS adsorption, while moderate catalyst loadings optimized light penetration and active site availability. Pareto analysis identified pH as the dominant factor (Fig. 6a), and response surface plots (Fig. 6b) indicated optimal removal at low pH and moderate-to-high TiO₂ loadings. Under optimized conditions (1.45 g L⁻¹ TiO₂, pH 4.0), PFOS (100 μ g L⁻¹) degradation reached 83% after 8 h, with a predicted maximum oxidation of 86% and an initial rate of 0.64 h⁻¹ (Fig. 6c).

Sansotera *et al.* studied PFOA photomineralization on commercial P25 TiO₂, monitoring TOC and fluoride release and

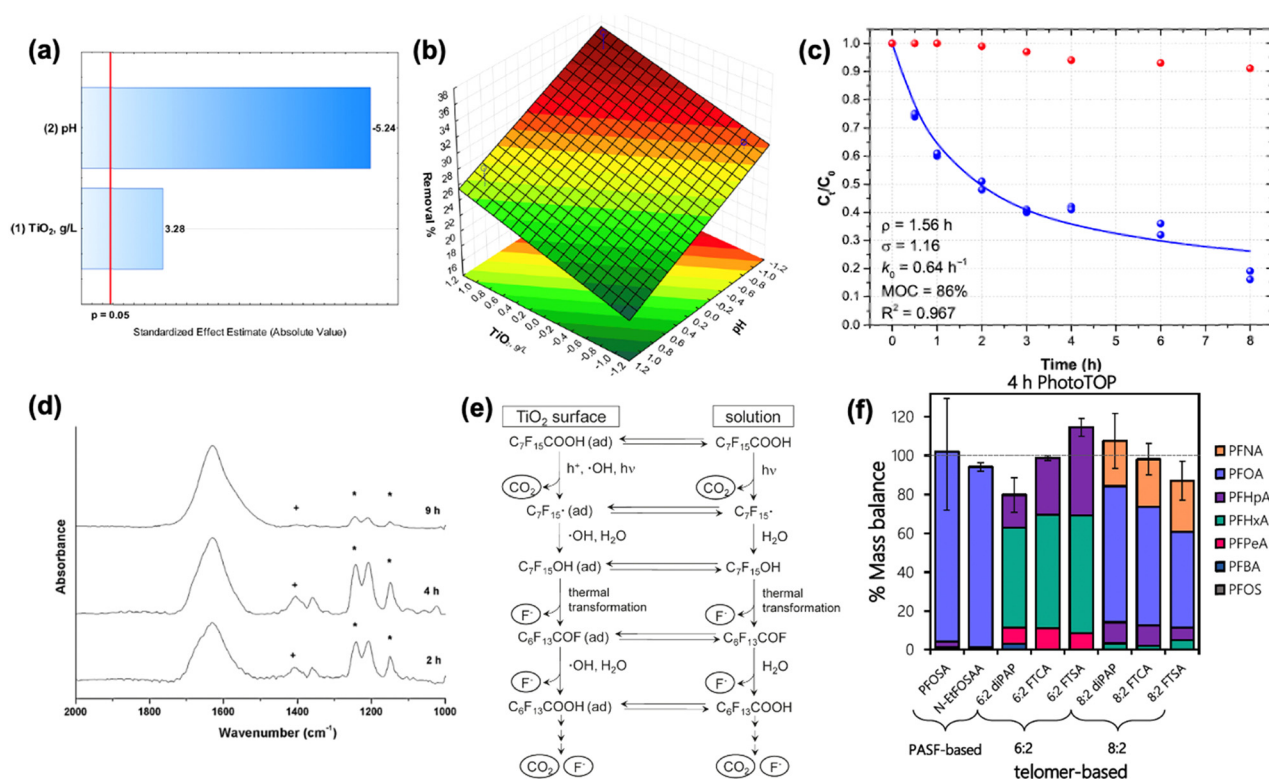


Fig. 6 Optimization of PFOS removal using TiO₂/UV photocatalysis via response surface methodology (RSM): (a) Pareto chart showing the relative effects of suspension pH and TiO₂ dosage on PFOS removal; bars crossing the significance line ($p = 0.05$) indicate statistically significant factors, highlighting pH as the dominant parameter, (b) response surface plot highlighting maximum removal at low pH with moderate catalyst loading, (c) time-dependent PFOS degradation measured by HPLC-MS/MS: (blue dots) TiO₂/UV photocatalysis, (red dots) direct photolysis. Reproduced from ref. 198 with permission from Elsevier BV, copyright 2021; (d) FT-IR spectra of TiO₂ during PFOA photodegradation: early spectra (2–4 h) show adsorption of PFOA and intermediates via C–F and carboxylate vibrations, while signals decrease after 9 h, reflecting progressive mineralization. Reproduced from ref. 199 with permission from Elsevier BV, copyright 2014; (e) stepwise decomposition of PFOA under UV-visible light, showing direct photolysis and TiO₂-assisted photocatalysis. PFOA undergoes sequential C–C cleavage, F⁻ elimination, and hydrolysis to form shorter-chain perfluorocarboxylic acids, ultimately mineralizing to CO₂ and F⁻. Reproduced from ref. 200 with permission from American Chemical Society, copyright 2011; (f) mass balance of representative PFAA precursors after 4 h of TiO₂/UV treatment, showing chain-length-dependent PFOA distributions. Reproduced from ref. 201 with permission from American Chemical Society, copyright 2022.²⁰¹



characterizing the photocatalyst by XPS and XRD.¹⁹⁹ The reaction followed pseudo-first-order kinetics ($k_{\text{app}} = 0.033\text{--}0.057\text{ h}^{-1}$) *via* Kolbe decarboxylation, producing C7 radicals, shorter-chain PFCAs, and HF. FT-IR spectra (Fig. 6d) indicated adsorption *via* carboxylate and C-F interactions within 2–4 h, with transient perfluorinated alcohols at 1210 cm^{-1} , followed by signal reduction after 9 h as mineralization progressed. XPS indicated early-stage surface fluorine (85–90%) with mineralization plateauing at $\sim 32\%$ and fluoride release at $\sim 29\%$. XRD revealed stable anatase ($\sim 25\text{ nm}$) and partially amorphized rutile ($47 \rightarrow 33\text{ nm}$), highlighting that surface interactions, radical dynamics, and adsorption, rather than crystal structure, control efficiency.

The UV irradiation type strongly affects TiO_2 performance. Low-pressure (LPUV, 254 nm) lamps provide narrow spectra, whereas medium-pressure (MPUV, 200–400 nm) lamps deliver higher photon flux and broader irradiation.²⁰² Ochiai *et al.*²⁰⁰ achieved near-complete degradation of 5 mM PFOA using 1.5 wt% P25 under MPUV (250–375 nm, $\sim 600\text{ mW cm}^{-2}$ at 254 nm), with pseudo-first-order kinetics ($k = 8.6 \times 10^{-2}\text{ dm}^3\text{ h}^{-1}$), $\sim 6\times$ faster than direct photolysis and $5\text{--}100\times$ faster than other catalysts (*e.g.*, tungstic heteropoly acid 2.1×10^{-3} and $\beta\text{-Ga}_2\text{O}_3$ $1.7 \times 10^{-2}\text{ dm}^3\text{ h}^{-1}$).^{203,204} Fig. 6e describes the TiO_2 -assisted photocatalytic pathway where MPUV light initiates C–C bond cleavage in PFOA, leading to sequential shortening of perfluoroalkyl chains and eventual mineralization into CO_2 and F^- .

PhotoTOP is a TiO_2 -based platform for PFAS precursor characterization that operates under mild conditions ($\sim 60\text{ }^\circ\text{C}$) without added chemicals, enabling direct LC-MS analysis with minimal matrix interference.²⁰¹ It uses anatase TiO_2 ($\sim 390\text{ nm}$, $\text{pH}_{\text{pzc}} 3.6$) to generate steady-state hydroxyl radicals ($\bullet\text{OH}$, $1.1\text{--}1.5 \times 10^{-12}\text{ M}$), allowing controlled oxidation that preserves the original perfluoroalkyl chain lengths. This contrasts with the higher-temperature TOP assay ($85\text{ }^\circ\text{C}$) and persulfate-based methods, which often produce ultrashort PFCAs such as trifluoroacetic acid due to harsher conditions and stronger chain-shortening potential.^{201,205,206} PhotoTOP quantitatively converted eight PFAA precursors into PFCAs with mass balances of 82–115% after 4 h (Fig. 6f), performing reliably across complex matrices including soil extracts (15 mg L^{-1} dissolved organic carbon (DOC)), PFAS-coated papers, and technical mixtures. Unlike traditional methods, it also allows direct oxidation of solids, capturing non-extractable precursors, although this proceeds approximately $10\times$ slower than extract oxidation. Compared to literature-reported TOP assays and chemical oxidation approaches, PhotoTOP offered milder, more selective oxidation, higher tolerance to matrix effects, and mechanistic insight into precursor-PFCA transformations ($R^2 = 0.88$). Its main limitation is the need for a controlled UV setup, but this enables reproducible $\bullet\text{OH}$ generation and predictable oxidation kinetics. PhotoTOP provided a practical and mechanistically informative approach that bridges analytical characterization and photocatalytic treatment of PFAS precursors, complementing existing methods in the literature.

6. TiO_2 modification and hybrid strategies

Pristine TiO_2 generates reactive species capable of degrading PFAS; however, low visible-light absorption, rapid $\text{e}^- \text{--} \text{h}^+$ recombination, and the high stability of C–F bonds limit its performance. To address these challenges, TiO_2 modifications and hybrid strategies aim to enhance light harvesting, charge separation, and surface reactivity. Approaches include metal and non-metal doping, single-atom incorporation, semiconductor coupling, immobilization on supports, and hybrid system design, all intended to maximize photocatalytic potential for persistent contaminants.

6.1. Modified TiO_2 systems

Metal and non-metal doping of TiO_2 is a widely employed strategy to enhance photocatalytic activity under visible light, addressing the intrinsic wide bandgap of anatase TiO_2 ($\sim 3.2\text{ eV}$) that limits UV-only activation^{207–210} (Fig. 7). Metal doping introduces mid-gap states, improves visible-light absorption, promotes charge separation, and generates oxygen vacancies that facilitate PFAS adsorption and reactive oxygen species formation.²¹¹ Transition metals (Fe, Co, and Cu) create Ti^{3+} centers and oxygen defects; noble metals (Ag, Au, and Pt) enhance interfacial charge transfer and suppress $\text{e}^- \text{--} \text{h}^+$ recombination; rare-earth metals (La^{3+} , Ce^{3+} , Gd^{3+} , and Nd^{3+}) serve as electron traps and increase surface area.^{211–215} Dopants are incorporated *via* sol-gel, hydrothermal, electrospinning, or surface impregnation methods.^{216,217} Non-metal doping extends visible-light activity without metal toxicity by introducing states above the valence band and narrowing the bandgap. Substitutional N ($\sim 0.14\text{ eV}$ above the VB) and interstitial N ($\sim 0.73\text{ eV}$) reduce the bandgap to $\sim 2.6\text{ eV}$, while S lowers it from 3.203 eV to $2.753\text{--}2.545\text{ eV}$ depending on concentration.^{218–221} Excessive doping can create recombination centers, necessitating careful optimization.²²² Although, these modifications are extensively studied in general photocatalysis, their application for PFAS degradation on TiO_2 remains emerging. Early reports suggest that such modifications enhance visible-light absorption, promote charge separation, and increase ROS generation, thereby potentially improving degradation kinetics and defluorination efficiency.

Estrillan *et al.*²²³ demonstrated visible-light photocatalytic degradation of PFOA using Fe and Nb co-doped TiO_2 (Fe:Nb- TiO_2) *via* sol-gel synthesis. XRD confirmed retention of the anatase phase with reduced crystallite size (11.4 nm), suppressing anatase-to-rutile transformation. Under UV-vis irradiation (200–600 nm) with 0.1 mM PFOA, pH 4.3, and a catalyst loading of 0.5 g L^{-1} , Fe:Nb- TiO_2 achieved nearly double the degradation efficiency of SG- TiO_2 , whereas AO- TiO_2 P25 showed minimal activity. Enhanced performance was attributed to larger surface area ($> 120\text{ m}^2\text{ g}^{-1}$ *vs.* $\sim 114\text{ m}^2\text{ g}^{-1}$ for SG- TiO_2), Fe-induced bandgap narrowing, and Nb sites that trap photogenerated electrons, suppressing recombination and extending visible-light absorption. Maximum PFOA removal occurred at pH 4 due to electrostatic attraction between negatively charged perfluorooctanoate anions and positively charged TiO_2 , facilitating valence band hole-driven oxidation. At neutral or higher pH,



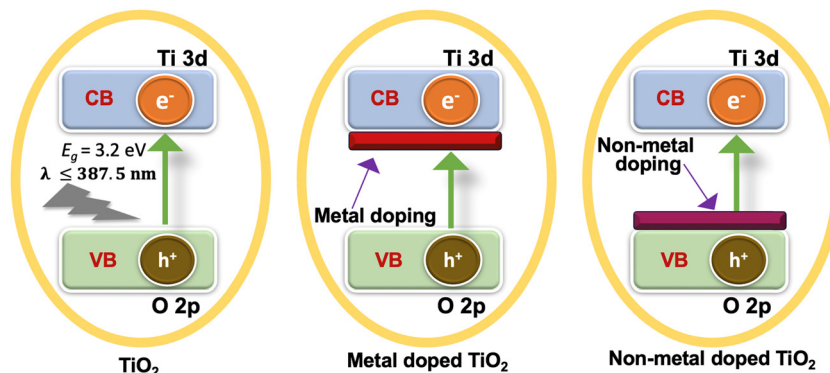


Fig. 7 Schematic illustrating the effects of metal and non-metal dopants on the properties and activity of TiO_2 -based photocatalysts.

surface speciation shifts to Ti-OH or Ti-O^- , weakening adsorption, while the Fe-TiO_2 point of zero charge (pzc 7.2) and PFOA's low pK_a (2.8) limit adsorption and photocatalytic activity under alkaline conditions.^{186,187}

UV-activated TiO_2 modified with transition metals such as Fe and Cu was studied for PFOA degradation (Fig. 8a–c).²²⁴ XRD characterization revealed mixed anatase-rutile phases, with Fe-TiO_2 containing zero-valent Fe and Cu-TiO_2 showing Cu^0 and Cu_2O . Under UV irradiation (0.5 g L^{-1} catalyst, pH 5, 298 K, 12 h), Cu-TiO_2 achieved 91% PFOA decomposition with 19% defluorination, outperforming UV/TiO_2 (14% decomposition) and UV/Fe-TiO_2 (69% decomposition, 9% defluorination). Enhanced activity of Cu-TiO_2 arises from stronger electron trapping *via* Cu^0/Cu^+ species, suppressing e^-/h^+ recombination more effectively than $\text{Fe}^{2+}/\text{Fe}^0$ (standard reduction potentials: $+0.34 \text{ V}$ vs. -0.44 V), increasing valence band hole availability.²²⁵ Cu deposition also introduces localized energy levels in the TiO_2 bandgap, enhancing UV absorption, while redox cycling of Cu facilitates electron transfer and perfluoroalkyl radical formation. Studied by Li *et al.*,²²⁶ noble-metal-doped TiO_2 (Pt, Pd, and Ag) was investigated for PFOA degradation. Unlike transition metals, noble metals with high work functions efficiently capture electrons, suppress e^-/h^+ recombination, and enhance valence band hole-driven oxidation, with localized surface plasmon resonance (LSPR) extending absorption into the visible range.^{227,228} Li *et al.*²²⁶ reported Pt-, Pd-, and Ag-modified TiO_2 (5 nm metal nanoparticles on 20–40 nm TiO_2 aggregates) for PFOA degradation. At pH 3, 60 mg L^{-1} PFOA and 0.5 g L^{-1} catalyst, Pt- TiO_2 , achieved 100% decomposition and 34.8% defluorination after 7 h UV irradiation, with the pseudo-first-order rate constant $12.5\times$ higher than that of pure TiO_2 . Pd- TiO_2 and Ag- TiO_2 achieved 94.2% and 57.7% decomposition with defluorination of 25.9% and 8.1%, respectively. Larger work functions of Pt (5.65 eV), Pd (5.55 eV), and Ag (4.26 eV) form Schottky barriers, efficiently trapping conduction-band electrons. Degradation proceeds *via* h_{VB}^+ -driven stepwise CF_2 cleavage, producing shorter-chain PFCAs and fluoride ions (Fig. 8d and e). Rate constants increase with higher initial PFOA concentrations, demonstrating sustained photoactivity under elevated pollutant loads.

Pb-modified TiO_2 has explored as an effective non-noble alternative. Pb introduced *via* photodeposition maintains the

anatase-rutile framework, with XRD confirming Pb^0 , PbO , and PbO_2 incorporation without lattice disruption.²²⁹ Pb species act as electron traps, enhancing charge separation. Under UV irradiation, Pb- TiO_2 exhibited a pseudo-first-order rate constant of 0.5136 h^{-1} , $32.5\times$ higher than that of UV/TiO_2 (0.0158 h^{-1}), achieving nearly complete PFOA decomposition (99.9%) in 12 h, with a half-life of 1.3 h compared to 43.9 h for pristine TiO_2 . Acidic conditions (pH 3) and O_2 -rich environments further promoted decomposition *via* $\bullet\text{OH}$ formation, while N_2 sparging drastically reduced activity (Fig. 8f). Mechanistic analysis (Fig. 8g) indicates sequential C–C cleavage, $\bullet\text{OH}$ attack, and chain shortening to CO_2 and F^- , with Pb acting as an efficient electron trap. The optimal Pb: TiO_2 ratio (2:100) and catalyst loading ($0.5\text{--}1.0 \text{ g L}^{-1}$) maximized degradation efficiency. Compared to noble-metal doped- TiO_2 , Pb- TiO_2 leverages acidic, oxygenated conditions to achieve faster kinetics and more complete degradation, highlighting the potential of strategic heavy-metal doping for PFAS remediation. Noble-metal doped TiO_2 catalysts (Pt, Pd, and Ag) achieve faster and more complete PFOA degradation with higher defluorination than transition-metal doped TiO_2 , highlighting the effect of the dopant type on both reaction kinetics and partial mineralization. Pb- TiO_2 also shows high activity, reaching 99.9% degradation and 22.4% defluorination in 7 h,²²⁹ comparable to Pt- TiO_2 but slightly lower in defluorination. Among transition metals, Cu- TiO_2 shows moderate performance, while Fe- TiO_2 is less effective, and Fe:Nb- TiO_2 mainly promotes stepwise chain-shortening.^{223,228}

6.2. Single-atom catalysis (SAC) on TiO_2

Single-atom catalysts (SACs) have gained considerable attention in photocatalysis due to maximal metal atom utilization, uniform active sites, and unique reaction pathways compared to conventional nanoparticles.^{230–232} TiO_2 -based SACs are particularly attractive for PFAS remediation, as isolated metal atoms can modulate charge separation, electronic structure, and interfacial interactions, enhancing pollutant degradation.^{233,234}

Weon *et al.* (2021) demonstrated the integration of facet-engineered TiO_2 with single-atom Pt (Pt_1) cocatalysts.⁵² Anatase TiO_2 crystals with {001} and {101} facets were synthesized, with fluoride ions stabilizing {001} ($\sim 80\%$ surface area) and APTMS anchors selectively immobilizing PtCl_6^{2-} on {101}, followed by



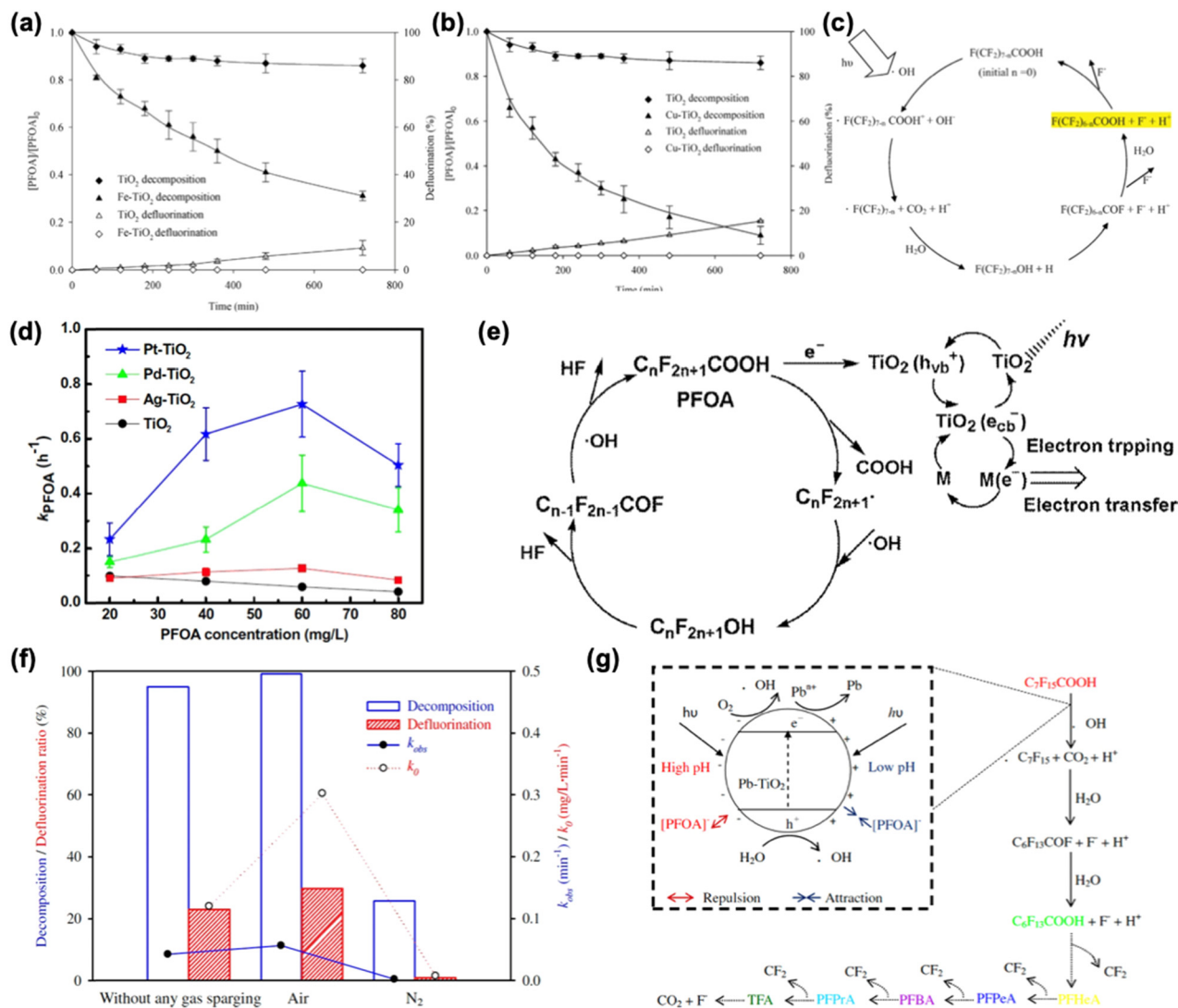


Fig. 8 Photocatalytic degradation of PFOA using TiO₂-based materials: (a) comparison of degradation and defluorination efficiency: bare TiO₂ (~14% degradation in 12 h), Fe-TiO₂ (~69% degradation, 9% defluorination), (b) Cu-TiO₂ (~91% degradation, 19% defluorination), (c) schematic of PFOA decomposition under UV/TiO₂: •OH-mediated C–C bond cleavage and stepwise defluorination to shorter-chain PFCAs and F[−], with Fe or Cu doping enhancing •OH generation and electron–hole separation. Reproduced from ref. 224 with permission from Elsevier BV, copyright 2015; (d) rate constants for PFOA degradation using pure TiO₂ and noble-metal-doped TiO₂; Pt and Pd show superior electron-trapping effects, (e) mechanism of PFOA degradation on TiO₂ and M-TiO₂: UPLC-MS showed stepwise CF₂ loss, mainly forming PFHpA (up to 19.1 mg L^{−1}). Pt-TiO₂ and Pd-TiO₂ accelerated PFHpA generation (16–19 mg L^{−1} in 3–5 h) vs. Ag-TiO₂ (9.7 mg L^{−1} in 7 h). About 80% F[−] remained in solution, with ~20% lost to adsorption/gas. Decomposition followed Kolbe decarboxylation and HF elimination, yielding shorter PFCAs, CO₂, and F[−]. Reproduced from ref. 226 with permission from Elsevier BV, copyright 2016; photocatalytic decomposition of PFOA by Pb-TiO₂: (f) PFOA decomposition and defluorination at different pH values and under different atmospheres: highest at pH 3 (~99%/30%) with air; low under N₂ (~26%/1%), (g) mechanistic pathway: UV-excited Pb-TiO₂ generates perfluoroalkyl radicals that undergo stepwise HF elimination and hydrolysis, forming shorter-chain PFCAs and finally CO₂ and F[−]. Pb improves efficiency by trapping electrons and reducing electron–hole recombination. Reproduced from ref. 229 with permission from Elsevier BV, copyright 2016.

photoreduction to atomically dispersed Pt₁ (~0.2 nm, confirmed by HAADF-STEM). This design exploited intrinsic band-driven charge separation; electrons migrated to {101} and holes to {001}, ensuring site-specific Pt₁ placement and maximizing electron utilization. Pt₁/facet-engineered TiO₂ exhibited substantially more •OH generation than PtNP/TiO₂ and showed ~15× higher PFOA degradation (Fig. 9a). The single-atom design facilitated (i) efficient electron transfer from the TiO₂ conduction band to Pt₁, (ii) selective proton reduction forming Pt-H^{δ−} species, and (iii) hydrogen spillover onto TiO₂ to generate reactive

Ti-H^{δ+} species that cleave C–F bonds, forming Ti–F (Fig. 9b). XPS confirmed Ti–F formation, and fluorine mass balance indicated ~58% retention in Ti–F bonds, with minimal free F[−] or HF. This accumulation of Ti–F bonds represents a key catalyst deactivation pathway, as surface fluorination progressively blocks active Ti–OH sites and suppresses interfacial redox reactions. Importantly, Weon *et al.* demonstrated that this fluoride-induced deactivation is fully reversible. A mild NaOH washing step converted inactive Ti–F back to catalytically active Ti–OH (>Ti–F + OH[−] ↔ >Ti–OH + F[−]), restoring photocatalytic activity without Pt loss



or aggregation. This regeneration strategy directly addresses long-term durability concerns by decoupling high defluorination efficiency from permanent catalyst poisoning. Moreover, the atomically dispersed Pt_1 remained stable during reaction and regeneration cycles, indicating strong metal-support interactions and resistance to sintering or leaching, two common degradation routes in Pt nanoparticle-based systems.

As an alternative to noble-metal modification strategies, non-precious single-atom catalysts (SACs) have gained increasing attention. In this context, Bi single-atom catalysts (Bi-SACs) on TiO_2 , synthesized *via* green, UV-assisted methods, exhibit uniform metal dispersion and strong photocatalytic performance.²³⁵ N-Bi/ TiO_2 (from $\text{Bi}(\text{NO}_3)_3$) and Cl-Bi/ TiO_2 (from BiCl_3 forming BiOCl nanoclusters) were investigated for PFOA degradation. N-10Bi/ TiO_2 achieved $\sim 85\%$ defluorination under xenon lamp irradiation in 4 h, while Cl-10Bi/ TiO_2 achieved $\sim 76\%$ (Fig. 9c–e). Pristine TiO_2 and Fe- or Pd-modified TiO_2 showed negligible activity. Enhanced performance of Bi- TiO_2 arises from improved charge separation (photocurrent, EIS), side-on PFOA adsorption, and Bi \cdots F interactions that polarize C–F bonds, as supported by DRIFTS, DFT, and FDTD simulations.²³⁶ Unlike Pt_1/TiO_2 systems that proceed *via* reductive hydrodefluorination, Bi- TiO_2 operates

through oxidative-defluorination, enabling rapid breakdown of PFOA and shorter-chain PFCAs. N-10Bi/ TiO_2 also demonstrated excellent recyclability, maintaining $>90\%$ PFOA removal over four cycles with only a slight decrease in defluorination ($\sim 65\%$). These results establish Bi- TiO_2 as an efficient, stable, and sustainable non-noble-metal SAC for PFAS remediation.

6.3. Hybrid photocatalysts

Hybrid photocatalysts have been widely investigated for PFAS remediation, wherein TiO_2 is integrated with complementary materials to tailor its physicochemical and photochemical characteristics and broaden its functional scope. This section discusses key hybridization strategies studied for PFAS degradation, including coupling TiO_2 with other semiconductors or oxides to form heterojunctions or Z-scheme architectures, use of carbon-modified TiO_2 to facilitate electron transport and pollutant adsorption, and the integration of advanced material hybrids.

6.3.1. TiO_2 coupled with other semiconductors or oxides.

TiO_2 -based heterojunctions have been explored as a means to modify charge-transfer pathways and light-response characteristics for PFAS degradation.^{237,238} Coupling TiO_2 with semiconductors such as Sb_2O_3 , BiOBr , BN, or ReS_2 enables the formation

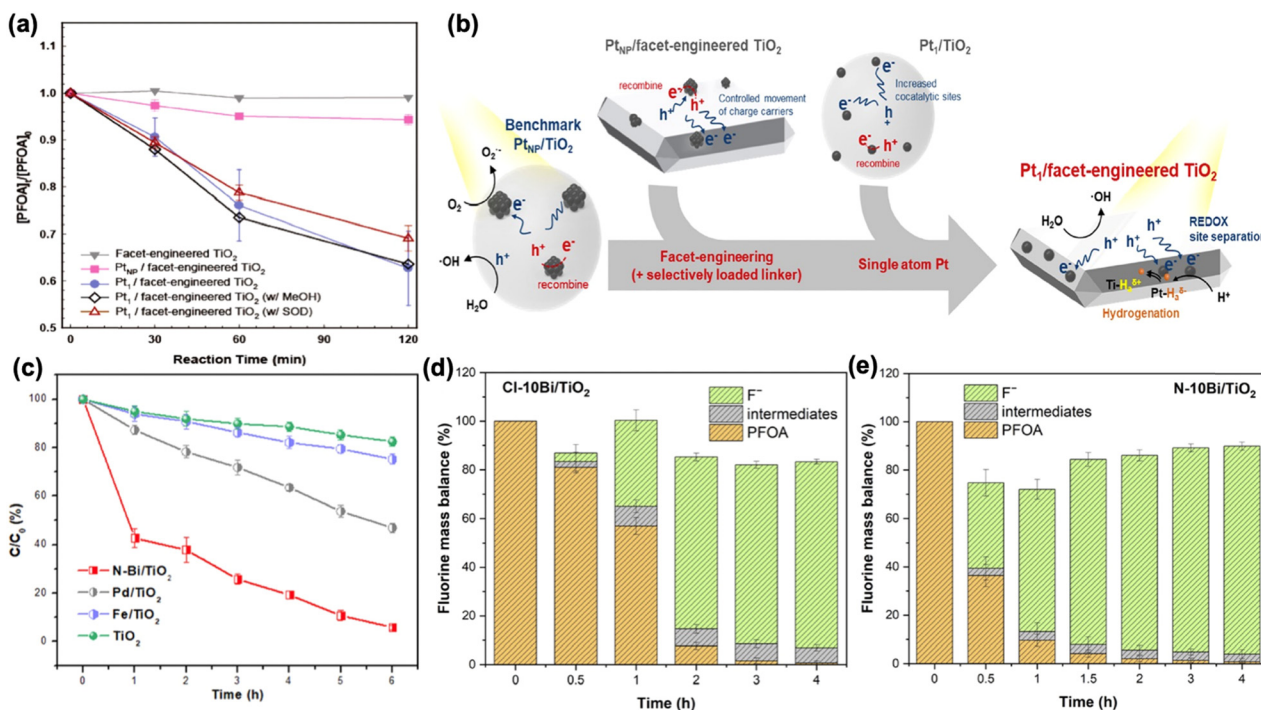


Fig. 9 Photocatalytic hydrodefluorination of PFOA using Pt-loaded TiO_2 : (a) facet-engineered TiO_2 shows negligible PFOA degradation, Pt nanoparticle/ TiO_2 improves performance moderately, and single-atom Pt_1 /facet-engineered TiO_2 achieves the highest degradation, with the pseudo-first-order rate constant $\sim 15\times$ higher than that of PtNP/TiO_2 , demonstrating efficient C–F bond hydrodefluorination. (b) Single-atom Pt_1/TiO_2 and Pt_1 /facet-engineered TiO_2 show higher PFOA degradation than Pt nanoparticles due to efficient hydrogen spillover. Ti–F bonds form (58% of fluorine), with negligible free fluoride. Performance decline from Ti–F accumulation is reversible *via* NaOH. Facet engineering with Pt_1 shifts the pathway from $\text{O}_2^{\bullet-}$ to surface hydrogen species, enabling effective hydrodefluorination. Reproduced from ref. 52 with permission from American Chemical Society, copyright 2021,⁵² photocatalytic defluorination of PFOA by Bi single-atom-loaded TiO_2 . (c) Pure TiO_2 shows low PFOA degradation ($\sim 15\%$) and defluorination ($\sim 2\%$). Fe or Pd doping slightly improves activity, while Bi single atoms (Bi SACs) significantly enhance defluorination (up to 70%), (d) under a xenon lamp, N-10Bi/ TiO_2 achieves complete PFOA removal within 2 h and high defluorination ($\sim 85\%$) after 4 h, outperforming Cl-10Bi/ TiO_2 , (e) short-chain PFCAs (PFHpA, PFHxA, and PFPeA) are detected as intermediates. N-10Bi/ TiO_2 shows rapid defluorination and maintains $>65\%$ activity over four cycles, demonstrating stability and practical potential. Reproduced from ref. 235 with permission from American Chemical Society, copyright 2023.



of type-II, p-n, and S-scheme heterojunctions, promoting spatial separation of charge carriers and expanded utilization of visible light. These hybrid systems provide additional electron- and hole-driven pathways that help degrade persistent PFAS.

Yao *et al.* developed mesoporous $\text{Sb}_2\text{O}_3/\text{TiO}_2$ heterojunctions for PFOA degradation.²³⁹ SEM and TEM revealed bowl-like anatase TiO_2 particles (~ 10 nm) uniformly embedded with Sb_2O_3 nanocrystals, producing red-shifted light absorption and a narrowed bandgap ($3.30 \rightarrow 2.91$ eV). At 10 ppm PFOA and 0.25 g L^{-1} catalyst, 3%- $\text{Sb}_2\text{O}_3/\text{TiO}_2$ achieved 81.7% removal in 120 min, with the pseudo-first-order rate constant $4.2 \times$ faster than P25 ($12.6 \times 10^{-3} \text{ min}^{-1}$ vs. $6.3 \times 10^{-3} \text{ min}^{-1}$, Fig. 10a). ESR, PL, and TR-PL analyses identified $\text{O}_2^{\bullet-}$ and h^+ as dominant

reactive species, while $\bullet\text{OH}$ was negligible, indicating a shift from conventional hydroxyl-mediated pathways (Fig. 10b).

BiOBr-modified P25 (P25/BiOBr) forms a p-n heterojunction, facilitating efficient charge separation.²⁴⁰ Under simulated solar irradiation, P25/BiOBr achieved 99.7% PFOA degradation within 100 min, outperforming P25 ($< 1\%$), BiOBr alone (13.4%), and commercial In_2O_3 (16.8%, Fig. 10c).²⁴² ATR-FTIR and adsorption studies indicated unidentate binding of PFOA to Bi^{3+} , enhancing surface adsorption ($q_m = 21.94 \text{ mg g}^{-1}$) and direct hole-mediated oxidation. Mechanistically, photogenerated holes dominated, with negligible contribution from $\bullet\text{OH}$, electrons, or superoxide anions, consistent with BiOBr's VB energy (1.99 V vs. NHE) being insufficient for water oxidation (Fig. 10d).^{243,244} In real water from Tangxun Lake (pH 3.5), degradation was efficient but

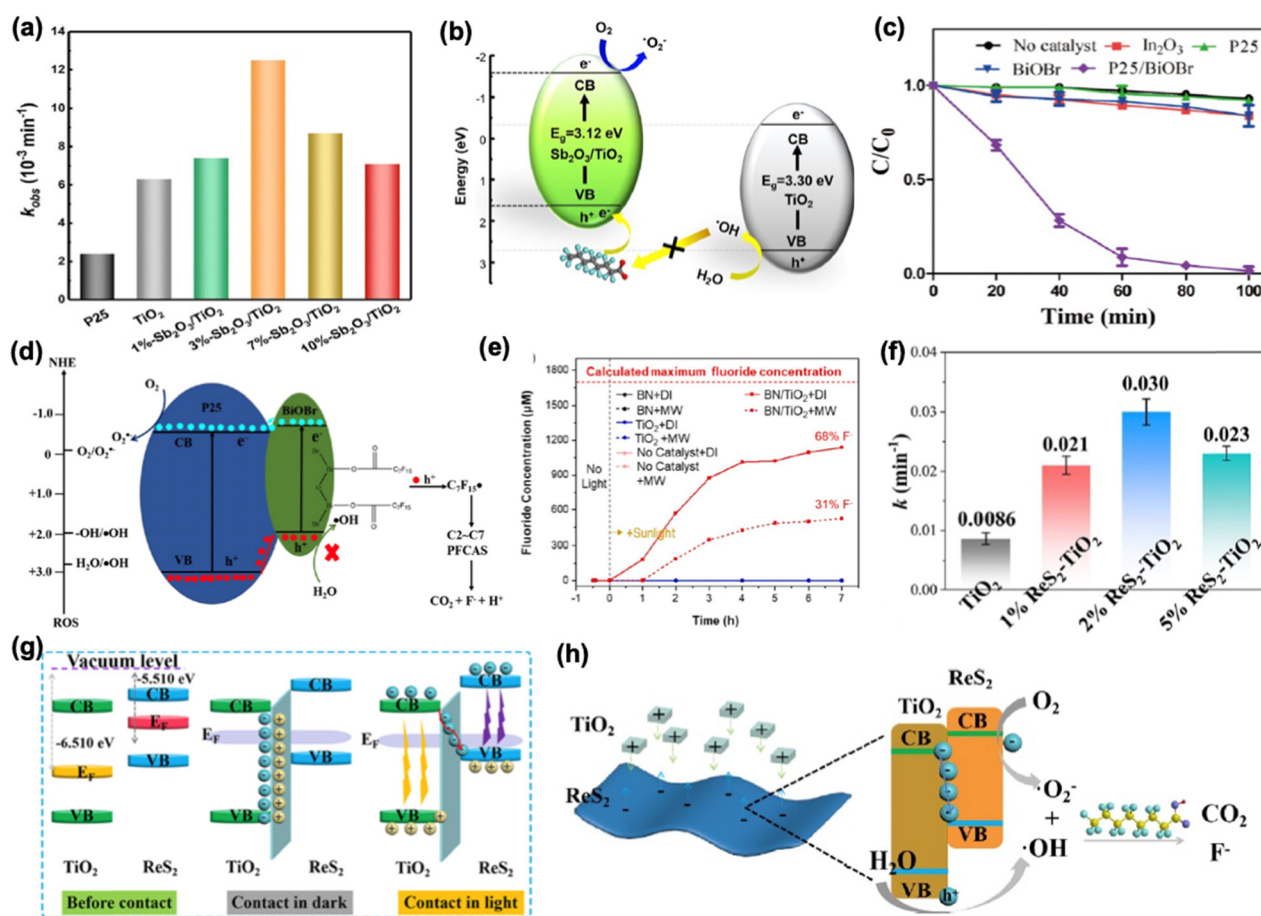


Fig. 10 Photocatalytic degradation of PFOA: (a) comparison of calculated degradation rate constants for P25, TiO_2 , and TiO_2 modified with 1%, 3%, 7%, and 10% Sb_2O_3 , (b) schematic showing how the 3%- $\text{Sb}_2\text{O}_3/\text{TiO}_2$ heterojunction enhances photocatalytic PFOA degradation. Reproduced from ref. 239 under the Creative Commons Attribution (CC BY), Frontiers, 2021; (c) PFOA degradation under simulated solar light, where P25/BiOBr achieved 99.7% removal in 100 min, significantly higher than that of BiOBr (13.4%), commercial In_2O_3 (16.8%), P25, or blank, attributed to its high adsorption capacity ($q_m = 21.94 \text{ mg g}^{-1}$), (d) proposed photodegradation pathway over P25/BiOBr: holes generated on P25 migrate to BiOBr, oxidizing adsorbed PFOA, followed by stepwise decarboxylation and hydrolysis, producing short-chain PFCAs and ultimately CO_2 and F^- . Reproduced from ref. 240 with permission from Elsevier BV, copyright 2022; (e) fluoride ion release profiles during PFOA degradation under natural sunlight irradiation using BN/TiO_2 , compared with controls. Reproduced from ref. 37 with permission from Elsevier BV, copyright 2022; (f) degradation rate constants for different $x\%$ $\text{ReS}_2/\text{TiO}_2$ samples, (g) proposed electron transfer mechanism in the $\text{ReS}_2-\text{TiO}_2$ S-scheme heterostructure, illustrating band bending and internal electric field formation driven by Fermi level differences, (h) proposed photocatalytic mechanism of the $\text{ReS}_2-\text{TiO}_2$ system under UV irradiation, showing charge transfer, oxygen vacancy trapping, radical generation ($\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$), and subsequent PFOA degradation. Reproduced from ref. 241 with permission from Elsevier BV, copyright 2025.



slowed at natural pH 6.8 due to reduced adsorption and competing ions (Cl^- , SO_4^{2-} , and NO_3^-) and NOM, low NO_3^- or humic acid ($\sim 10 \text{ mg L}^{-1}$) slightly enhanced removal (as NO_3^- can act as scavengers of electrons), while higher concentrations ($> 100 \text{ mg L}^{-1}$) inhibited it.²⁴⁵

The development of BN/TiO₂ composites advanced PFAS photocatalysis degradation.³⁷ Combining commercial TiO₂ (P25, 80 wt% anatase/20 wt% rutile, 21 nm) with hexagonal BN ($\sim 1 \mu\text{m}$) *via* simple calcination forms a type-II n-n heterojunction that promotes efficient interfacial charge separation.^{246,247} Ultraviolet photoelectron spectroscopy (UPS) and diffuse reflectance UV-vis (DR-UV) spectroscopy revealed valence band positions of -7.0 eV (TiO₂) and -6.9 eV (BN), with band gaps of 3.1 eV and 5.4 eV, respectively. This configuration allows TiO₂ photoexcitation under UV-C (254 nm) and UV-A (365 nm), while BN primarily facilitates e^- - h^+ separation. Transient photocurrent measurements showed $\sim 47\times$ and $\sim 70\times$ higher steady-state current for BN/TiO₂ relative to BN and TiO₂, indicating enhanced charge separation and reduced recombination. Under UV-A, BN/TiO₂ degraded 120 μM PFOA to $< 2.4 \mu\text{M}$ within 120 min ($t_{1/2} = 55 \text{ min}$), compared to 77 μM remaining with TiO₂ alone ($t_{1/2} \approx 350 \text{ min}$), achieving 37% *versus* 19% defluorination. Under UV-C, BN/TiO₂ further accelerated mineralization ($t_{1/2} = 13 \text{ min}$) and reached $> 50\%$ defluorination after 60 min, outperforming BN ($t_{1/2} = 10 \text{ min}$, 29% defluorination) and TiO₂ ($t_{1/2} = 80 \text{ min}$, 7% defluorination, Fig. 10e). BN/TiO₂ also showed practical advantages, requiring fluence doses of $\sim 4\text{--}8 \text{ J cm}^{-2}$ and $\text{EE}/O_{\text{output}}$ values of 102 and 253 $\text{kWh m}^{-3} \text{ order}^{-1}$ under UV-C and UV-A, representing $> 10\times$ improved energy efficiency compared to TiO₂.

Chen *et al.* constructed an S-scheme ReS₂-TiO₂ heterostructure *via* electrostatic self-assembly, combining oppositely charged semiconductors to enhance interfacial electron transfer and suppress recombination.²⁴¹ Transmission and electron microscopy (TEM) and elemental mapping confirmed uniform Re, S, Ti, and O distribution, while XPS and Raman analyses revealed increased oxygen vacancies (21 to 26%) and surface -OH groups (13 to 17%), boosting radical generation. Photocatalytic tests demonstrated that 2% ReS₂-TiO₂ achieved 98% PFOA removal with $\sim 75\%$ defluorination in 120 min under UV, surpassing TiO₂ (62%) and ReS₂ alone. Radical trapping and ESR studies identified $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ as dominant species, with ReS₂ coupling significantly enhancing their formation. *In situ* XPS and DFT calculations elucidated the S-scheme mechanism: an internal electric field drives electron transfer from TiO₂ to ReS₂ in the dark, while upon illumination, TiO₂ CB electrons migrate to the ReS₂ VB, promoting charge separation, extending carrier lifetime, accelerating electron transfer, and increasing active site availability (Fig. 10f-h).^{248,249} For TiO₂ heterojunctions, 3% Sb₂O₃/TiO₂ achieved 81.7% PFOA degradation in 2 h,²³⁹ BN/TiO₂ degraded 120 μM PFOA to $< 2.4 \mu\text{M}$ in 120 min with 37% defluorination under UV-A and $> 50\%$ under UV-C in 60 min,³⁷ and ReS₂-TiO₂ (2 wt%) removed 98% PFOA with $\sim 75\%$ defluorination in 120 min.²⁴¹

6.3.2. Carbon-based hybrid photocatalysts. Carbon materials enhance TiO₂ photocatalysis by improving charge transfer,

suppressing electron-hole recombination, and increasing pollutant adsorption.²⁵⁰⁻²⁵⁴ π -Conjugated structures act as electron reservoirs, enabling rapid electron migration, while the high surface areas of carbon nanotubes, graphene, and activated carbon concentrate pollutants near catalytic sites. This synergy boosts reactive oxygen species generation and extends TiO₂'s light response into the visible range.

Fe/TNTs@AC demonstrated a "concentrate-and-destroy" mechanism, achieving 91.3% PFOA removal in 4 h under UV irradiation, outperforming TNTs@AC (23.8%), non-calcined Fe/TNTs@AC (68.7%), and calcined TNTs@AC (83.3%) (Fig. 11a).²⁵⁵ Fe modification and calcination enhanced defluorination ($\sim 62\%$), 1.5-4 \times higher than that of other materials. Optimal calcination (550 $^\circ\text{C}$) and 1 wt% Fe loading maximized performance. Fe/TNTs@AC adsorbed $\sim 99\%$ of PFOA over pH 4-11 within 2 h, with $\alpha\text{-Fe}_2\text{O}_3/\text{TNTs}$ interacting electrostatically with the carboxylate head and AC providing hydrophobic and anion- π interactions with the tail.²⁵⁶ Adsorption orientation shifted from side-on (acidic/neutral) to tail-on (alkaline), slightly reducing defluorination at pH ≥ 9 . Reusability tests confirmed stable adsorption ($> 99\%$) and $\sim 60\%$ defluorination over six cycles, with minimal Fe ($< 1.7 \text{ mg L}^{-1}$) and no Ti leaching. Mechanistic studies revealed h^+ -driven oxidation as dominant, with $\bullet\text{OH}$ mediating stepwise defluorination of perfluoroalkyl radicals, $\bullet\text{O}_2^-$ was negligible (Fig. 11b). Fukui index and ESP analyses identified the carboxylate head as the primary reactive site, supporting the proposed degradation pathway.²⁵⁷

Titanate nanotubes (TNTs) have been further modified to enhance photocatalytic PFAS degradation through metal doping and carbon integration.²⁵⁸⁻²⁶¹ Gallium-doped TNT-activated carbon composites (Ga/TNTs@AC) demonstrated synergistic adsorption-photocatalysis for PFOS removal. Both TNTs@AC and 2%Ga/TNTs@AC achieved near-complete PFOS adsorption within 10 min, far exceeding bare AC (equilibrium in 120 min) despite its higher surface area.²⁵⁸ Langmuir analysis indicated a maximum surface-area-normalized adsorption capacity of 0.225 mg m^{-2} for 2%Ga/TNTs@AC, $\sim 2.1\times$ higher than that of AC, highlighting the combined effects of Ga doping and AC in creating electrostatic, hydrophobic, and π -anion binding sites.^{260,261} Under UV irradiation, 2%Ga/TNTs@AC achieved 75% PFOS degradation and 66.2% defluorination within 4 h, significantly outperforming TNTs@AC (13.1%/6.2%) and AC alone (Fig. 11c), with the underlying mechanism illustrated in Fig. 11d. The system exhibited broad pH tolerance (3.5-10.5), with alkaline conditions favoring $\text{O}_2^{\bullet-}$ generation and defluorination. XPS and EPR confirmed Ga³⁺ induced oxygen vacancies that acted as electron traps, improving charge separation and ROS formation, supported by reduced PL emission.

Indium-doped TNT-AC composites (In/TNTs@AC) were developed for PFOA remediation.²⁵⁹ Characterization showed an interwoven TNT-AC framework, with In present mainly as In₂O₃ and minor In⁰ phases.^{262,263} XRD confirmed anatase retention with reduced interlayer spacing, while FTIR and N₂ adsorption indicated partial surface-group removal and slightly reduced pore volume, favoring PFOA adsorption. Batch tests achieved $> 99\%$ PFOA removal within 30 min *via* hydrophobic



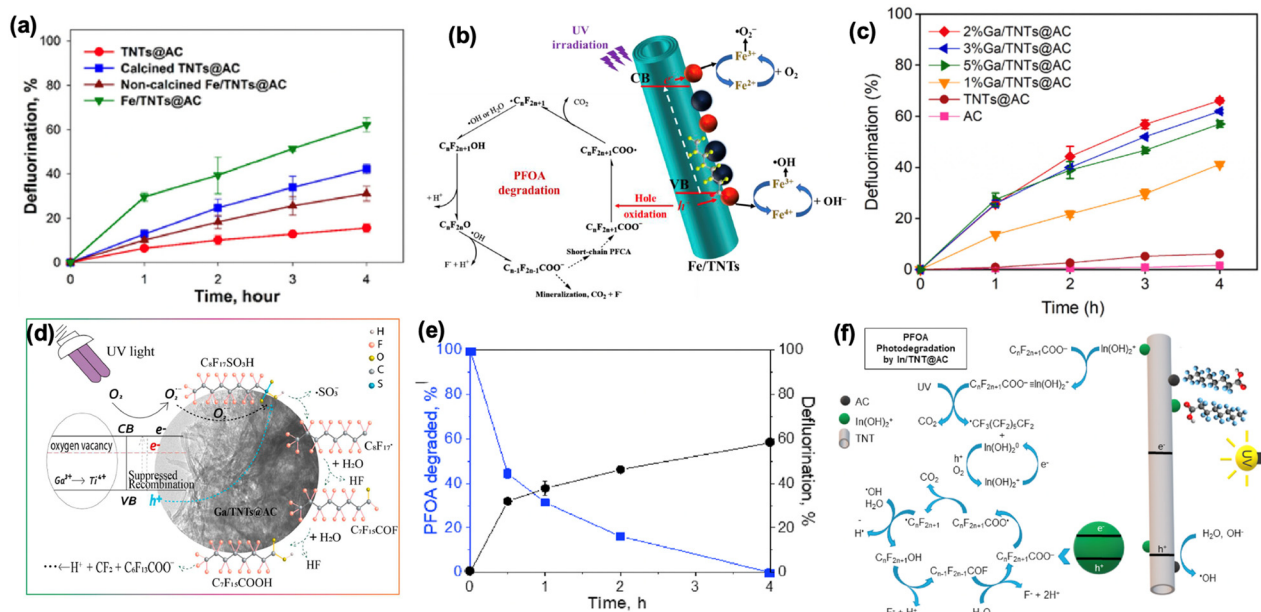


Fig. 11 (a) Photocatalytic defluorination of PFOA, showing $\sim 62\%$ conversion of organic fluorine to F^- by Fe/TNTs@AC under UV irradiation, significantly higher than that of TNTs@AC and other controls, (b) proposed photocatalytic degradation mechanism of PFOA on iron (hydroxide-impregnated) nanoparticles under UV irradiation, showing adsorption, hole/electron generation, radical formation, and stepwise defluorination via photo-Kolbe-like decarboxylation. Reproduced from ref. 255 with permission from Elsevier BV, copyright 2020; (c) kinetics of PFOA defluorination for neat AC, TNTs@AC, and Ga/TNTs@AC with varying Ga content under UV irradiation, (d) proposed mechanism for enhanced solid-phase photocatalytic degradation and defluorination of PFOS by Ga/TNTs@AC, highlighting multi-point adsorption, Ga-induced oxygen vacancies, charge separation, and generation of reactive species (h^+ and $O_2^{\bullet-}$). Reproduced from ref. 258 with permission from Elsevier BV, copyright 2021;²⁵⁸ (e) Photodegradation and defluorination of PFOA pre-adsorbed on In/TNTs@AC under UV irradiation, showing rapid degradation ($>50\%$ in 30 min) and $\sim 60\%$ defluorination after 4 h, (f) proposed stepwise photocatalytic degradation and defluorination pathways of PFOA on In/TNTs@AC, highlighting dual adsorption, In-facilitated redox cycling, and formation of perfluoroalkyl intermediates during UV irradiation. Reproduced from ref. 259 under the Creative Commons CC-BY licence, Elsevier BV, 2022.

and electrostatic/Lewis acid–base interactions at In_2O_3 sites.²⁶⁴ Under UV irradiation, In/TNTs@AC achieved nearly complete PFOA degradation within 4 h with $\sim 60\%$ defluorination, outperforming AC, TNTs@AC, and In_2O_3 @AC due to synergistic adsorption and enhanced charge separation via heterojunction formation (Fig. 11e and f). TNT-based composites exhibit clear dopant-dependent behavior in PFAS degradation.^{255,258,259} Fe modification promotes redox-driven pathways and enhances defluorination, Ga doping improves oxygen-vacancy-mediated charge separation favoring sulfonated PFAS removal, and In doping enables combined hydrophobic and Lewis acid–base adsorption with In_2O_3 heterojunction-assisted photocatalysis, favoring carboxylated PFAS. Overall, dopant selection governs charge transport, vacancy chemistry, and PFAS-specific interactions, providing a mechanistic basis for rational design of TNT-based photocatalysts.

Multi-walled carbon nanotubes (MWCNTs) serve as supports to improve adsorption and charge separation.²⁶⁵ TiO_2 -MWCNT composites synthesized via sol–gel with varying TiO_2 :MWCNT ratios were tested under 365 nm UV (8 h) with 30 mg L^{-1} PFOA. Adsorption equilibrium on MWCNTs occurred within 30 min ($\sim 18\%$ PFOA). A 5 : 1 TiO_2 -MWCNT composite achieved 89% PFOA degradation, surpassing P25 (37%) and physical mixtures (60%) (Fig. 12a). Optimized 10 : 1 loading yielded 94% degradation, whereas 20 : 1 caused aggregation and reduced efficiency.

TiO_2 photocatalysis is significantly boosted through integration with reduced graphene oxide (rGO), which has been studied for the degradation of various pollutants.^{266–269} Ruiz *et al.* investigated TiO_2 -rGO composites for PFOA degradation under UV irradiation.²⁶⁶ While bare TiO_2 removed only $24 \pm 11\%$ of PFOA after 12 h, TiO_2 -rGO achieved $93 \pm 7\%$ removal under identical conditions (Fig. 12b), representing an ~ 4 -fold improvement. The enhanced activity is attributed to: (i) one-atom-thick rGO sheets that reduce light screening, (ii) efficient electron transfer from TiO_2 to rGO, and (iii) prolonged charge-carrier lifetimes, which enhance $\bullet OH$ and $O_2^{\bullet-}$ generation (Fig. 12c). Total organic carbon decreased by 62%, and 20% of fluorine was removed through combined adsorption (6.8%) and partial volatilization of short-chain products. Kinetic analysis revealed chain-length-dependent degradation: $k_{PFPEA} = 2.14\text{ h}^{-1} > k_{PFHXA} = 0.54\text{ h}^{-1} > k_{PFHPA} = 0.27\text{ h}^{-1} > k_{PFOA} = 0.163\text{ h}^{-1}$, indicating faster degradation of shorter-chain PFCAs. In subsequent studies, TiO_2 -rGO degraded both dichloroacetic acid (DCA) and PFOA, but complete mineralization occurred only for DCA, highlighting the strong recalcitrance of fluorinated compounds.²⁶⁸ Chowdhury *et al.* developed a synergistic Pb-doped TiO_2 /rGO system (TiO_2 -Pb/rGO) for PFOA remediation under UVC irradiation²⁶⁷ (Fig. 12d). The composite achieved 98% PFOA removal and 32% defluorination, surpassing TiO_2 -Pb, TiO_2 /rGO, and TiO_2 -Fe/rGO. Pb outperformed Fe for defluorination (34% vs. 15%) due to its more favorable standard



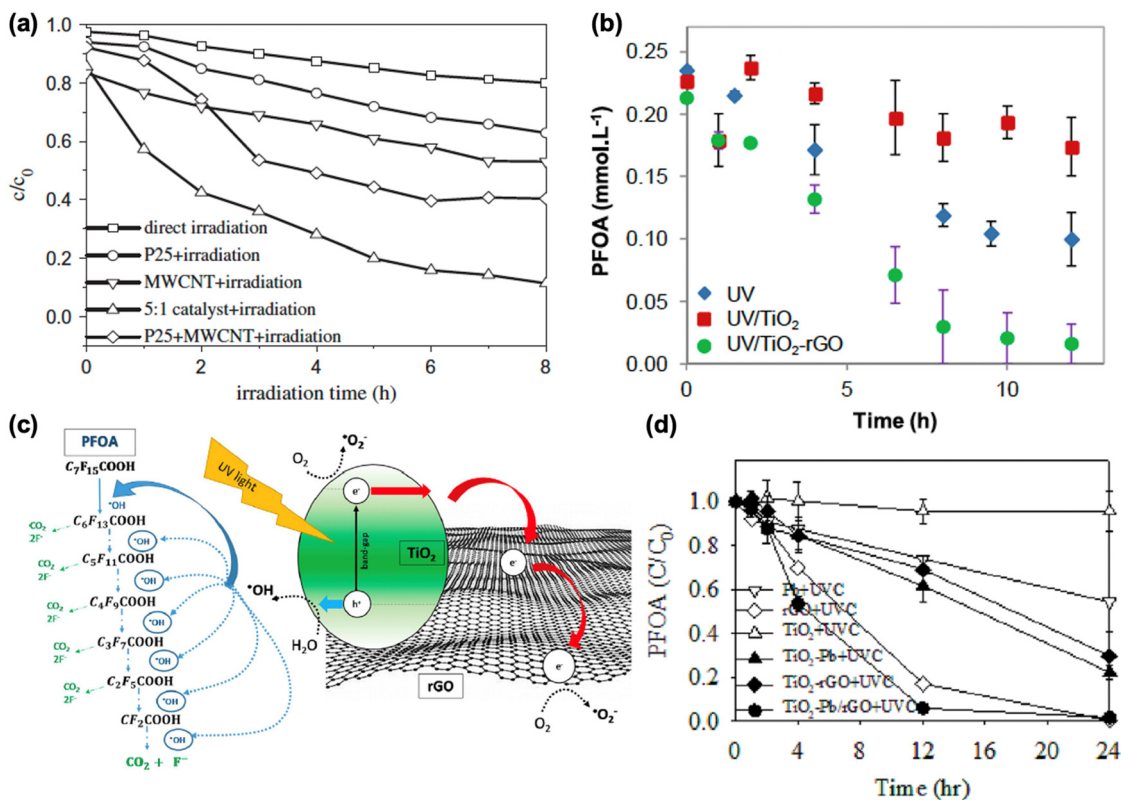


Fig. 12 Photocatalytic degradation of PFOA and PFOS over various TiO_2 -based and modified photocatalysts: (a) comparison with a physical mixture of P25 and MWCNTs (5 : 1). Reproduced from ref. 265 with permission from Elsevier BV, copyright 2012;²⁶⁵ (b) comparison of PFOA degradation after 12 h under UV irradiation using TiO_2 , TiO_2 -rGO composite, and GO control, showing enhanced removal with TiO_2 -rGO due to improved light penetration and reduced electron-hole recombination, (c) proposed photocatalytic degradation pathway of PFOA over TiO_2 -rGO, highlighting the role of rGO in enhancing charge separation, radical generation ($\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$), stepwise perfluoroalkyl cleavage, and eventual formation of CO_2 and F^- . reproduced from ref. 266 with permission from Elsevier BV, copyright 2018;²⁶⁶ (d) PFOA removal under UVC irradiation using TiO_2 , Pb, rGO, TiO_2 -Pb, TiO_2 /rGO, and TiO_2 -Pb/rGO, showing enhanced degradation with composite materials due to synergistic effects of rGO and Pb doping. Reproduced from ref. 267 with permission from Wiley, copyright 2023.

reduction potential. The TiO_2 -Pb/rGO system was effective under UVA, UVB, and UVC, with UVC slightly more efficient, achieving a low electrical energy per order (E_{EO}) of 4.05 kWh m^{-3} for 98% PFOA removal.

Ultra-small TiO_2 quantum dots (QDs) have been developed and uniformly distributed on supports to enhance photocatalytic efficiency by maximizing the active surface area.^{269–271} Sodium dodecyl sulfate (SDS) was used to regulate Ti^{3+} ion distribution, minimizing TiO_2 particle size. The resulting QDs ($\sim 2.55 \text{ nm}$) were assembled into three-dimensional sulfonated graphene (SG) aerogels, forming 3D SG- TiO_2 QD aerogels.²⁷² Compared to conventional TiO_2 nanoparticles (15–40 nm), these QDs exhibit enhanced photon absorption and reduced e^-h^+ recombination. Photocatalytic PFOA degradation followed first-order kinetics, with QDa (SG- TiO_2 QDs synthesized at higher SDS concentration) achieving the highest rate constant ($k_{\text{app}} = 1.898 \times 10^{-4} \text{ s}^{-1}$), outperforming QDb (SG- TiO_2 QDs synthesized at lower SDS concentration) ($1.530 \times 10^{-4} \text{ s}^{-1}$) and aggregated TiO_2 NPs ($9.283 \times 10^{-5} \text{ s}^{-1}$) (Fig. 13a). The synergistic combination of SG aerogels and TiO_2 QDs enhanced adsorption, promoted uniform QD dispersion, reduced band gap, and improved photogenerated charge utilization, enabling

persistent and high-efficiency PFAS degradation even in flow-through setups (Fig. 13b).

Carbon quantum dots (CQDs) have emerged as effective modifiers of TiO_2 photocatalysts, enhancing visible-light absorption and promoting efficient charge separation.^{275,276} High-purity CQDs synthesized *via* hydrothermal treatment of mussel shell biomass (MCQD) and electrochemical exfoliation of graphite rods (Exfol.CQD)²⁷³ were coupled with TiO_2 to form composite photocatalysts. Photocatalytic experiments under UVC and visible light demonstrated substantially improved degradation of perfluorooctanoic acid (PFOA) and short-chain PFCAs (C_3 – C_6). Stepwise decomposition of longer-chain PFCAs (*e.g.*, PFHxA- C_6 and PFPeA- C_5) to shorter intermediates (PFBA- C_4 and PFPrA- C_3) was observed, with higher intermediate concentrations under UVC irradiation (PFHxA $11.5 \mu\text{g L}^{-1}$, PFPeA $11.9 \mu\text{g L}^{-1}$) than under visible light (PFHxA $9.8 \mu\text{g L}^{-1}$, PFPeA $8.2 \mu\text{g L}^{-1}$), reflecting more rapid generation of reactive species at higher photon energies. Corresponding defluorination efficiencies reached 32% (visible) and 34.5% (UVC) for Exfol. CQD/ TiO_2 , compared to 11.6% and 21.8% for bare TiO_2 . Photocurrent and IMVS/IMPS analyses confirmed faster electron transfer ($\tau_t = 0.317 \text{ ms}$) and longer hole lifetimes ($T_R = 35.9 \text{ ms}$), highlighting the role of CQDs in charge



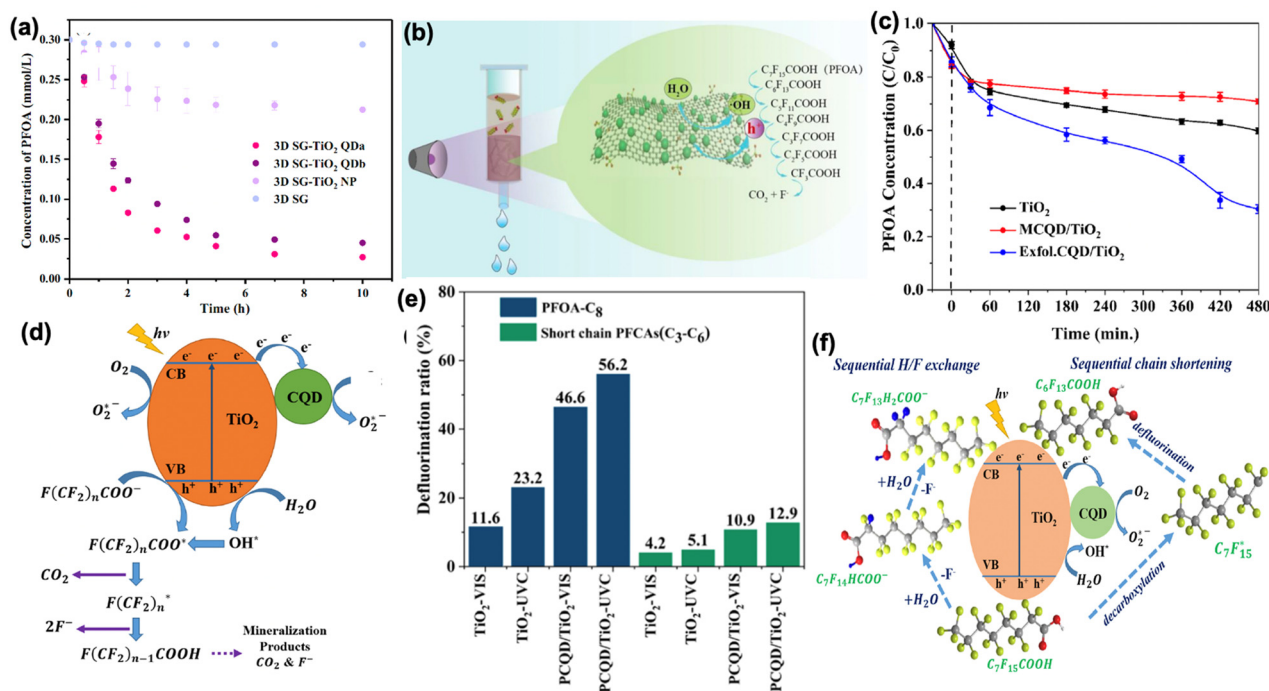


Fig. 13 (a) PFOA degradation profiles and simulated concentrations over time for 3D SG-TiO₂ QDa, 3D SG-TiO₂ QDb, 3D SG-TiO₂ NP, and 3D SG, showing faster kinetics for smaller TiO₂ QDs and supporting stepwise formation of shorter-chain PFCAs, (b) proposed mechanism for PFOA removal by 3D SG-TiO₂ QDa, showing combined adsorption on the hydrophobic aerogel surface and photocatalytic degradation via h⁺-induced and •OH-mediated pathways, leading to stepwise formation of shorter-chain PFCAs and fluoride release. Reproduced from ref. 272 with permission from Elsevier BV, copyright 2020; (c) photodegradation of PFOA over TiO₂, Exfol.CQD/TiO₂, and MCQD/TiO₂ under UVC (200–280 nm). Exfoliated CQDs enhance electron transfer, reduce electron-hole recombination, and improve photocatalytic efficiency compared to bare TiO₂. (d) proposed mechanism for PFOA decomposition using TiO₂ and CQD/TiO₂ photocatalysts. Upon light irradiation, electron-hole pairs are generated; holes in the valence band directly oxidize PFOA, while electrons in the conduction band participate in reactive oxygen species formation, enabling stepwise defluorination and formation of shorter-chain PFCAs. Reproduced from ref. 273 with permission from Elsevier BV, copyright 2025; (e) defluorination efficiency of PFOA and short-chain PFCAs (C₃–C₆) under UVC and visible light using TiO₂ and PCQD/TiO₂ photocatalysts. The PCQD/TiO₂ composite showed significantly higher defluorination percentages (46.6–56.2% for PFOA and 10.9–12.9% for short-chain PFCAs) compared to pristine TiO₂, (f) PFOA degradation over PCQD/TiO₂ proceeds via two main pathways: chain shortening, where reactive holes and radicals break C–C bonds to form shorter-chain PFCAs, and H/F exchange, where α–C–F bonds are sequentially replaced by hydrogen, releasing fluoride ions. Reactive oxygen species (•OH and O₂•⁻) generated by the photocatalyst drive these processes. Reproduced from ref. 274 with permission from Elsevier BV, copyright 2025.

separation. Fig. 13c shows improved PFOA photodegradation by CQD/TiO₂ under UVC due to enhanced charge separation, while Fig. 13d illustrates a mechanism involving direct hole oxidation and ROS-driven stepwise defluorination.

Similarly, peanut-shell biomass-derived CQDs (PCQD/TiO₂) extended TiO₂'s photoresponse from UV to visible light and reduced the band gap from 3.04 to 2.92 eV, acting as electron reservoirs and further enhancing e⁻/h⁺ separation.²⁷⁴ PFOA and other long-chain PFCAs degraded into shorter intermediates, with defluorination efficiencies significantly improved (PFOA: 56.2% UVC, 46.6% visible vs. 23.2% and 11.6% for bare TiO₂) (Fig. 13e). Both Exfol.CQD and PCQD composites exhibited stepwise PFOA degradation driven by superoxide (•O₂⁻), hydroxyl radicals (•OH), and photogenerated holes, maintaining stable performance over multiple cycles. Fig. 13f illustrates the mechanism: extended light absorption, improved e⁻-h⁺ separation, and reactive radical generation drive chain shortening, decarboxylation, and H/F exchange, achieving efficient mineralization. Among the three CQDs, PCQD/TiO₂ demonstrates the highest overall efficiency, achieving 67.2% degradation of long-chain

PFOA under UVC and 48.5% under visible light, while also effectively degrading short-chain PFCAs such as PFHxA (41.3%) and PFPeA (52.1%). Exfol.CQD/TiO₂ performs comparably for long-chain PFOA (69% UVC, 50% visible) but is less effective for short-chain PFCAs (PFHxA 40%, PFPeA 35%, PFBA 31.6%, and PFPPrA 21.6%). In contrast, mussel shell-derived CQDs (MCQD)/TiO₂ consistently exhibits the lowest activity (PFOA 29% UVC, 20% visible) with limited short-chain PFOA data. This quantitative comparison underscores that both the CQD precursor and synthesis method critically influence TiO₂ photocatalytic performance, with biomass-derived PCQDs offering a sustainable and broadly effective approach for PFAS remediation under both UVC and visible light.

6.3.3. Emerging hybrid systems. Supporting materials have been explored to enhance TiO₂ photocatalysis by improving catalyst stability, dispersion, and charge transport, leading to more effective utilization of photogenerated charge carriers.^{277–281} Among these, MXenes and zeolites exemplify distinct strategies for augmenting TiO₂ performance in PFAS degradation. MXenes, two-dimensional transition metal carbides and nitrides, combine

high conductivity, tunable surface chemistry, and layered architecture, enabling rapid electron transfer and heterojunction formation with TiO_2 .²⁷⁷ Hydrophilic surfaces and interlayer expansion enhance nanoparticle interaction, light utilization, and accessibility of active sites.

In one approach, hydrothermally synthesized MXene/ TiO_2 composites demonstrated a layered structure with TiO_2 nanoparticles anchored on MXene sheets, as confirmed by SEM, XRD, and XPS.²⁸² These composites coupled rapid adsorption with photocatalysis: PFOA adsorption reached equilibrium

within 30 min ($q_m \approx 16.06 \text{ mg g}^{-1}$), following pseudo-second-order kinetics and Langmuir isotherms, with efficiency strongly influenced by pH. Under UV irradiation, MXene/ TiO_2 achieved 94.6% degradation and 58.4% defluorination within 9 h, surpassing UV alone, UV/MXene, or UV/ TiO_2 systems (Fig. 14a). The Schottky barrier at the MXene- TiO_2 interface facilitated hole transfer, improving e^- - h^+ separation and extending catalyst durability. Comparative analysis with advanced photocatalytic systems including MXene nanosheets, Ti_4O_7 /MXene, COFs/MOFs and ZIF-67/Au-PCN reveals that the MXene/ TiO_2 system

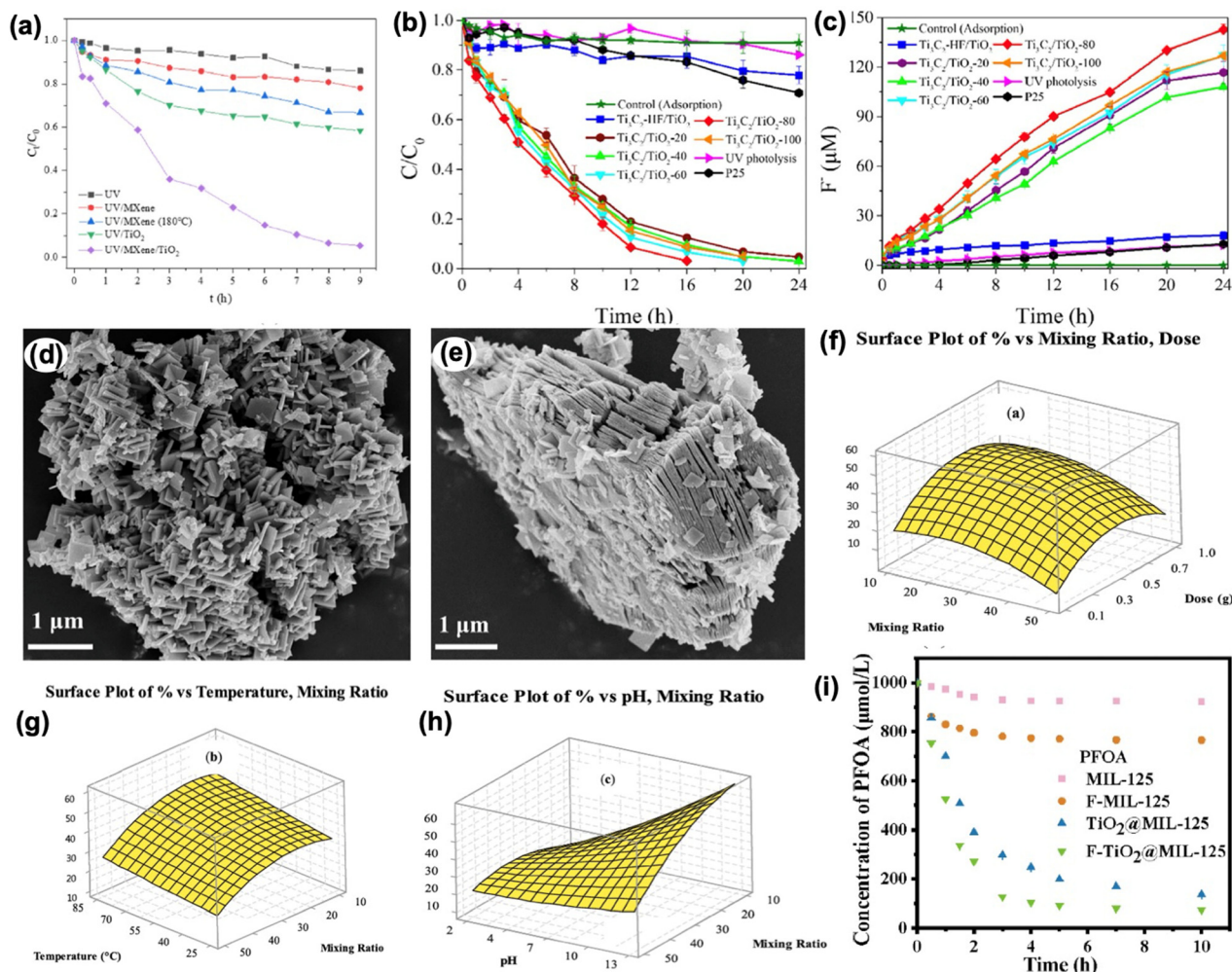


Fig. 14 (a) Photocatalytic degradation of PFOA under different systems: UV alone, MXene, hydrothermally treated MXene (180 °C), TiO_2 , and MXene/ TiO_2 composite. The MXene/ TiO_2 composite achieved the highest degradation (94.6%) due to enhanced light absorption and improved electron-hole separation, while UV alone showed minimal PFOA removal (13.96%). Reproduced from ref. 282 with permission from Elsevier BV, copyright 2025; photocatalytic degradation of PFOA using $\text{Ti}_3\text{C}_2/\text{TiO}_2$ -based catalysts: (b) PFOA removal under adsorption, UV photolysis, Ti_3C_2 -HF/ TiO_2 , P25, and $\text{Ti}_3\text{C}_2/\text{TiO}_2$ -80, (c) fluoride ion (F^-) generation and defluorination efficiency for the same systems, (d) TiO_2 distribution within Ti_3C_2 -DES showing intercalation into interlayers, (e) TiO_2 growth on the Ti_3C_2 -HF surface for comparison. The intercalation strategy ($\text{Ti}_3\text{C}_2/\text{TiO}_2$ -80) significantly enhances both PFOA degradation (>99.9%) and defluorination (49%) compared to conventional TiO_2 systems. Reproduced from ref. 283 with permission from Elsevier BV, copyright 2020; three-dimensional RS (response surface) diagrams illustrating the optimal operating conditions for maximum treatment efficiency: (f) effect of catalyst dosage (0.5–0.7 g) and zeolite mixing ratio (~10%) on efficiency; (g) influence of the zeolite ratio (~10%) and reaction temperature (up to 85 °C); (h) effect of the zeolite ratio (~10%) and pH (up to 13). The diagrams indicate that treatment efficiency improves with increasing zeolite ratio, increasing temperature, and higher pH under the specified conditions. Reproduced from ref. 284 with permission from Elsevier BV, copyright 2024; (i) PFOA degradation by MIL-125, F-MIL-125, TiO_2 @MIL-125, and F- TiO_2 @MIL-125 showed fastest kinetics for F- TiO_2 @MIL-125 with $k_{\text{app}} = 1.221 \times 10^{-4} \text{ s}^{-1}$, higher than that of other TiO_2 -based catalysts, while only TiO_2 @MIL-125 and F- TiO_2 @MIL-125 continued significant degradation after 2 h. Reproduced from ref. 66 with permission from Elsevier BV, copyright 2022.⁶⁶



has competitive advantages in persistent pollutant remediation. In a separate study, an intercalation strategy using deep eutectic solvents (DESSs) was developed to overcome the limited inter-layer spacing of Ti_3C_2 MXene, which typically hinders *in situ* TiO_2 crystal growth.²⁸³ The resulting Ti_3C_2 -DES exhibited expanded *c*-lattice parameters compared to the hydrofluoric acid (HF)-etched MXene, allowing greater water intercalation and more effective Ti atom oxidation. This promoted *in situ* TiO_2 crystal growth with exposed (001) and (101) facets, forming heterojunctions for enhanced charge separation. Combined with the high conductivity of the Ti_3C_2 substrate, this system enabled efficient carrier transport, achieving nearly 100% PFOA removal and 49% defluorination in 16 h. In contrast, Ti_3C_2 -HF/ TiO_2 and commercial P25 TiO_2 exhibited only modest efficiencies (22% removal, 12% defluorination, and 30% removal, 9% defluorination, respectively) (Fig. 14b and c), consistent with the morphological and mechanistic insights highlighted in Fig. 14d and e. Quantitatively, these results illustrate that faster C–F bond cleavage does not always correspond to higher overall PFOA removal. Altogether, these studies^{282,283} demonstrate that MXene/ TiO_2 hybrids can be engineered through hydrothermal or DES-driven strategies to maximize synergistic adsorption-photocatalysis, enhance charge separation, and significantly boost PFAS degradation, highlighting the versatility of MXenes as co-catalysts and structural supports for next-generation water treatment photocatalysts.

TiO_2 /zeolite nanocomposite materials were studied for photocatalytic pentafluoropropionic acid (PFPA) degradation, leveraging the complementary properties of both components.²⁸⁴ TiO_2 provides photocatalytic activity, while zeolites offer thermally and chemically stable scaffolds with high surface area and porous, hydrophobic structures that pre-concentrate pollutants, prevent nanoparticle aggregation, and, when modified (*e.g.*, alum-coated), enhance fluoride adsorption. Waste-derived Na–Y zeolite (68.7% purity) supported TiO_2 *via* sol–gel or hydrothermal methods, resulting in higher surface area ($273 \text{ m}^2 \text{ g}^{-1}$ *vs.* $46.3 \text{ m}^2 \text{ g}^{-1}$ for P25), reduced bandgap (2.75 eV *vs.* 3.28 eV), and preserved structural integrity (EDX Ti:Si:Al = 42.4:34.9:22.7). Systematic evaluation using ANOVA and response surface (RS) methodology identified pH (alkaline, pH 13) as the most influential factor, followed by dosage and the TiO_2 /zeolite ratio, with reaction temperature contributing moderately. The RS 3D plots (Fig. 14f–h) visually depict the interplay between these factors, highlighting the optimal ranges of dosage, zeolite ratio, temperature, and pH for maximum defluorination. Under these optimal conditions (0.5 g L^{-1} catalyst, 10% TiO_2 /zeolite, 85 °C, pH 13), PFPA defluorination reached 58.7–60.2%, with elevated surface area, pore structure, and charge properties promoting $\bullet\text{OH}$ -mediated degradation. These results highlight the synergy of TiO_2 and zeolite scaffolds and demonstrate a statistically validated approach for optimizing photocatalytic PFAS remediation.

Further advancement is represented by F- TiO_2 @MIL-125, integrating tailored adsorption and photocatalytic functionalities.⁶⁶ While MOF (MIL-125(Ti)) displayed smooth plate-like morphology (1 nm), TiO_2 @MIL-125 retained disc-like structure with smoother surfaces, and F- TiO_2 @MIL-125 preserved structural integrity with

superficial nano-debris despite fluorine functionalization. BET analysis showed a surface area decrease from $1201.71 \text{ m}^2 \text{ g}^{-1}$ (MIL-125) to $85.25 \text{ m}^2 \text{ g}^{-1}$ (F- TiO_2 @MIL-125), accompanied by an increase in pore diameter (2.13 → 12513.48 nm), favoring PFOA diffusion. F- TiO_2 @MIL-125 exhibited rapid adsorption (within 200 s) and superior monolayer capacities ($185.151 \mu\text{mol g}^{-1}$), outperforming MIL-125, F-MIL-125, and TiO_2 @MIL-125. Photocatalytic tests (Fig. 14i) under simulated sunlight demonstrated that only TiO_2 @MIL-125 and F- TiO_2 @MIL-125 sustained PFOA degradation beyond 2 h, with F- TiO_2 @MIL-125 achieving the highest rate constant ($K_{\text{app}} = 1.221 \times 10^{-4} \text{ s}^{-1}$), surpassing TiO_2 -rGO ($0.453 \times 10^{-4} \text{ s}^{-1}$) and fluorinated TiO_2 ($0.360 \times 10^{-4} \text{ s}^{-1}$). This enhanced performance was attributed to a narrowed bandgap (3.12 eV), redshifted absorption (460 nm), increased VB electron density, and improved electron–hole separation, as confirmed by UV-vis, Mott–Schottky, photocurrent, and EIS analyses. Mechanistically, PFOA removal involved $\text{F} \cdots \text{F}$ interactions for enrichment, followed by h^+ and $\bullet\text{OH}$ -mediated oxidation through stepwise defluorination. These studies highlight that MXenes, zeolites, and MIL-125-derived supports enhance TiO_2 photocatalysis *via* complementary mechanisms: adsorption, heterojunction-facilitated charge separation, structural stability, and tailored surface chemistry, achieving superior PFAS removal and defluorination compared to conventional TiO_2 catalysts.

6.4. Advanced photocatalysis-centric approaches

Recent developments in TiO_2 -based photocatalysis have focused on integrated strategies that improve overall performance by combining structural and functional modifications. Among these, photoelectrocatalysis (PEC) combines photocatalysis with an applied bias to accelerate interfacial reactions, while advanced oxidation processes (AOPs) exploit synergistic reactive oxygen species (ROS) pathways to mineralize persistent contaminants efficiently.^{285–288} Molecularly imprinted photocatalysts (MIPs) offer selective adsorption and degradation by creating tailored recognition sites for specific pollutants.^{289–291} This section highlights the mechanistic advantages and potential of these advanced strategies for PFAS degradation.

6.4.1. Photoelectrocatalysis. Photoelectrocatalysis (PEC) and bias-enhanced electrochemical photocatalysis (BEEP) demonstrate significant advantages over conventional photocatalysis for PFAS degradation. PEC improves photocatalytic performance by applying an external bias to semiconductor photocatalysts, enhancing e^- – h^+ separation, accelerating surface redox reactions, and promoting radical-mediated oxidation and defluorination.^{292–294} Laboratory studies using graphene oxide-deposited TiO_2 nanotube arrays (GO/TNAs) showed that defluorination efficiency depends on initial PFOA concentration and surface pH, with maximum degradation ($\sim 83\%$) at pH 3.²⁹⁵ Increasing the temperature from 25 °C to 75 °C accelerated degradation kinetics from 0.34 h^{-1} (83% in 4 h) to 1.63 h^{-1} (complete degradation in 2.5 h). Applying a 2 V external bias further improved removal efficiency to 97% by promoting charge separation, enhancing OH radical generation, and enabling anodic oxidation, although higher pH reduced efficiency due to competing OH^- adsorption (Fig. 15a).²⁹⁵ Similarly, bias-enhanced electrochemical photocatalysis (BEEP) demonstrates



significant PFAS degradation.²⁹⁶ BEEP combining UVA irradiation with a 2 V bias enabled complete mineralization of long-chain PFCAs (C_{13} – C_{17}) within 24 h, with shorter-chain intermediates progressively degraded (Fig. 15b and c). Sulfonamide-containing PFAS were fully removed, while PFOS and PFOA showed measurable defluorination ($\sim 15\%$ for PFOS in 24 h). Mass spectrometry confirmed PFOS degradation, with decreased molecular ion intensity during photocatalysis (Fig. 15d) and under BEEP treatment (Fig. 15e), providing molecular-level evidence of PFAS breakdown. The enhanced performance results

from reduced e^- – h^+ recombination, accelerated redox kinetics, and electrostatic attraction of PFAS to the biased TiO_2 surface, highlighting BEEP as an energy-efficient, scalable alternative to conventional treatments.

Field-relevant PEC studies further support these findings. In groundwater from the Veneto Region, Italy, the site of one of the largest PFAS environmental disasters in Europe, a total of 48 PFAS species, including long- and short-chain compounds, were monitored, with up to 9 species detected in the wells.²⁹⁷ The PEC treatment was carried out using immobilized TiO_2

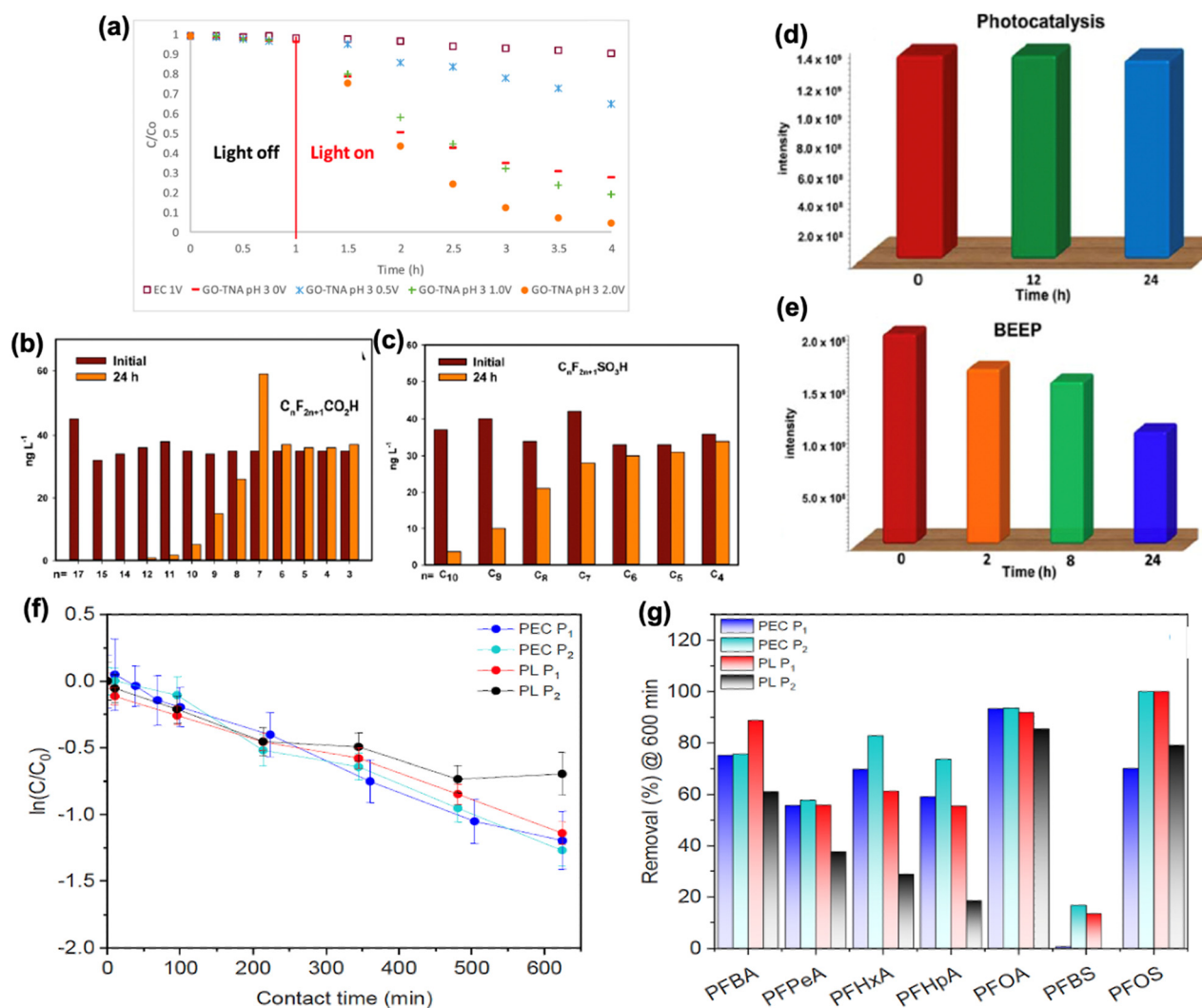


Fig. 15 (a) Photoelectrocatalytic degradation of PFOA on GO/TNAs under UV light was tested with external bias from 0 to 2.0 V. Degradation increased with applied potential due to enhanced electron transfer from TNAs to graphene oxide sheets. Reproduced from ref. 295 with permission from Elsevier BV, copyright 2018,²⁹⁵ photocatalytic degradation of PFAS using the BEEP reactor: (b) concentration changes of PFCAs after 24 h, showing complete removal of long chains (C_{12} – C_{17}) and progressive breakdown of shorter chains (C_{8} – C_{12}) into smaller intermediates, (c) removal of PFSAs, with the longest PFSAs (C_{10}) achieving 90% degradation, while shorter chains (C_{7} – C_{9}) show lower removal, (d) mass spectra of PFTeDA (C_{14}) during BEEP treatment, illustrating stepwise decarboxylation and formation of smaller PFCAs ($[C_8F_{11}]^-$ and $[C_6F_{13}]^-$), (e) MS spectra of PFOS (C_8) showing $\sim 30\%$ removal and 15% defluorination after 24 h, highlighting BEEP's efficiency in degrading both long- and short-chain PFAS, including resistant compounds like PFOS and PFOA. Reproduced from ref. 296 with permission from Royal Society of Chemistry, under CC BY-NC 3.0,²⁹⁶ effect of UV power and PFAS chain length on removal efficiency: (f) influence of UV intensity on PFOA removal: in photolysis (PL), reducing power from P1 to P2 decreased removal from 68% to 50%, whereas in photoelectrocatalysis (PEC), removal remained high (65–72%) due to the catalytic activity of the TiO_2 -coated mesh. (g) Removal of PFAS with different chain lengths under PL and PEC: in PL at P2, removal increased with decreasing chain length (PFHpA 18.5% \rightarrow PFBA 61%), while at P1, removal ranged 55–61% for PFHpA, PFHxA, and PFPeA and 89% for PFBA. In PEC, removal rates at P2 were equal or higher than at P1, demonstrating efficient degradation across all chain lengths. Reproduced from ref. 297 under the Creative Commons CC-BY 4.0.



photoanodes (TiO₂ film grown on titanium mesh by plasma electrolytic oxidation), achieved overall PFAS reduction of 63% in well 1 and 65% in well 2, with individual removal efficiencies ranging from 96% (PFOA) to 1% (PFBS).²⁹⁷ The average degradation order followed PFOA > PFHpA > PFHxA = PFPeA > PFBA for PFCAs and PFOS > PFHpS for PFSAs. Laboratory tests in ideal PFOA solutions confirmed that PEC degradation proceeds *via* decarboxylation followed by stepwise CF₂-unit loss, with transient formation of shorter-chain intermediates. Laboratory comparisons between photolysis (PL) and PEC under two UV lamp power settings (P1 = higher, P2 = lower) illustrate the advantages of bias-assisted PEC: as shown in Fig. 15f, reducing UV intensity from P1 to P2 decreased PL removal from 68% to 50%, while PEC removal remained stable or slightly increased, ranging from 65% to 72%.²⁹⁷ Fig. 15g shows that for individual PFCAs, PL removal strongly depended on the chain length and light intensity, whereas PEC maintained consistent or higher removal across all chain lengths regardless of UV power. These results indicate that PEC is less dependent on radiation density and that bias-assisted charge separation is a key driver of robust kinetics. In terms of operational efficiency, PEC was more energy-efficient than PL: EEO values were 36 kWh m⁻³ for PEC *versus* 46–59 kWh m⁻³ for PL, outperforming most other advanced oxidation processes and showing comparable performance to plasma and advanced reduction processes. PEC, including advanced configurations such as BEEP, has shown potential for both laboratory and field-relevant PFAS-contaminated waters, enabling high removal and defluorination rates while maintaining energy efficiency and stability under varying UV conditions. These studies also indicate the importance of non-target analyses to further elucidate reaction pathways and identify by-products, as well as the potential value of pilot-scale reactors for evaluating energy consumption and process feasibility.

6.4.2. TiO₂-based advanced oxidation processes (AOPs). TiO₂ photocatalysis has been combined with advanced oxidation processes (AOPs) to achieve higher pollutant removal efficiencies than TiO₂ alone.^{298–301} In these hybrid systems, the addition of oxidants such as H₂O₂, O₃, peroxymonosulfate (PMS), or related species promotes the formation of reactive oxygen species, leading to accelerated degradation and improved mineralization of persistent contaminants.

Photocatalytic ozonation represents a highly effective TiO₂-AOP strategy.^{302,303} Pairing TiO₂ with ozone generates additional •OH, complementing photocatalytic oxidation. Using this approach, 99.1% PFOA degradation and 44.3% defluorination were achieved within 4 h (Fig. 16a).³⁰⁴ TiO₂/PMS systems were evaluated for PFOA degradation under both visible and UV light.³⁰⁵ Under optimized conditions (0.25 g L⁻¹ TiO₂, 0.75 g L⁻¹ PMS, pH 3, 300 W visible light), 50 mg L⁻¹ PFOA was degraded nearly completely within 8 h (Fig. 16b), with a pseudo-first-order rate constant of 0.310 h⁻¹, approximately 11× higher than that of TiO₂ alone (0.028 h⁻¹). Scavenger studies indicated that sulfate radicals (SO₄•⁻) from PMS and photogenerated holes (h⁺) from TiO₂ were the primary reactive species. In real wastewater, PFOA removal decreased to 65% (influent) and 82% (effluent) in 8 h (*k* = 0.136 and 0.070 h⁻¹) due to coexisting organic compounds, highlighting matrix effects

(Fig. 16c). Under UV light (254 and 185 nm, 32 W), degradation reached nearly 100% within 1.5 h, reflecting higher catalyst absorbance and stronger photon energy. For comparison with other TiO₂-based systems, TiO₂/PMS exhibits the highest apparent kinetics (*k* = 1.09 h⁻¹),³⁰⁵ followed by Pt-modified TiO₂ (*k* = 0.726 h⁻¹) and Pd-modified TiO₂ (*k* = 0.438 h⁻¹), while Ag-modified TiO₂ shows the lowest reaction rate (*k* = 0.126 h⁻¹).²²⁶ This comparison reflects differences in kinetic performance among TiO₂-based systems when evaluated strictly by apparent rate constants.

Venkatesan *et al.*³⁰⁶ evaluated seven pilot-scale AOPs for PFAS and 1,4-dioxane removal from New York groundwater, including UV/TiO₂. While these AOPs transformed PFAS precursors, complete mineralization was not achieved, and concentrations of individual PFAS often increased due to precursor conversion. Specifically, average increases were observed for PFBS (≈405%, range 0–1220%), PFOA (≈14%, 0–48%), PFOS (≈13%, 3–25%), PFHxA (≈1%, -7 to 9%), PFHpA (≈3.8%, 0–9.5%), PFHxS (≈3.3%, -11 to 13%), and PFNA (≈2%, 0–5.2%) (Fig. 16d). These increases were dependent on UV and oxidant dose, indicating that hydroxyl radical-based AOPs primarily facilitated precursor transformation rather than full degradation. Importantly, at one site, PFOA concentrations exceeded the New York State drinking water standard (10 ng L⁻¹) after treatment, highlighting the importance of considering AOP-induced PFAS formation when designing treatment systems. These findings highlight the challenges associated with AOPs, including limited removal efficiency and the potential for increasing certain PFAS concentrations, which complicates water treatment and regulatory compliance.

Photocatalytic ozonation, combining WO₃/TiO₂ catalysts with ozone under UVA-visible light, has been applied for the removal of five PFAS (PFOA, PFHxS, PFBS, 6:2 FTS, and GenX) from water.³⁰⁷ Four catalysts with varying WO₃ contents (0, 1, 3, and 5 wt%) were synthesized and the 5 wt% WO₃/TiO₂ catalyst (TW5) exhibited optimal properties and achieved 82% methylene blue removal in model tests. PFAS degradation after 4 h remained low (ΣPFAS removal ≈16%, range 4–26%), with photocatalytic ozonation only marginally improving removal compared to photocatalysis alone (Fig. 16e). Photolysis and ozone photolysis were less effective, and ozonation alone had a negligible effect. These results demonstrate both the potential and current limitations of AOPs for PFAS removal, highlighting the need to optimize catalyst design and treatment conditions across multiple PFAS types.

6.4.3. TiO₂ nanotube arrays (TNAs) with molecularly imprinted polymers (MIPs). In environmental remediation, selectivity is critical when targeting trace pollutants in complex matrices containing multiple chemical species. While advanced technologies such as photocatalysis, adsorption, and membrane separation perform efficiently under laboratory conditions, their effectiveness often declines in real water due to interference from coexisting compounds.^{308–313} Components such as natural organic matter (NOM), dyes, pharmaceuticals, or metal ions can occupy active sites, scavenge reactive species, or alter solution chemistry, particularly when target pollutants are present at



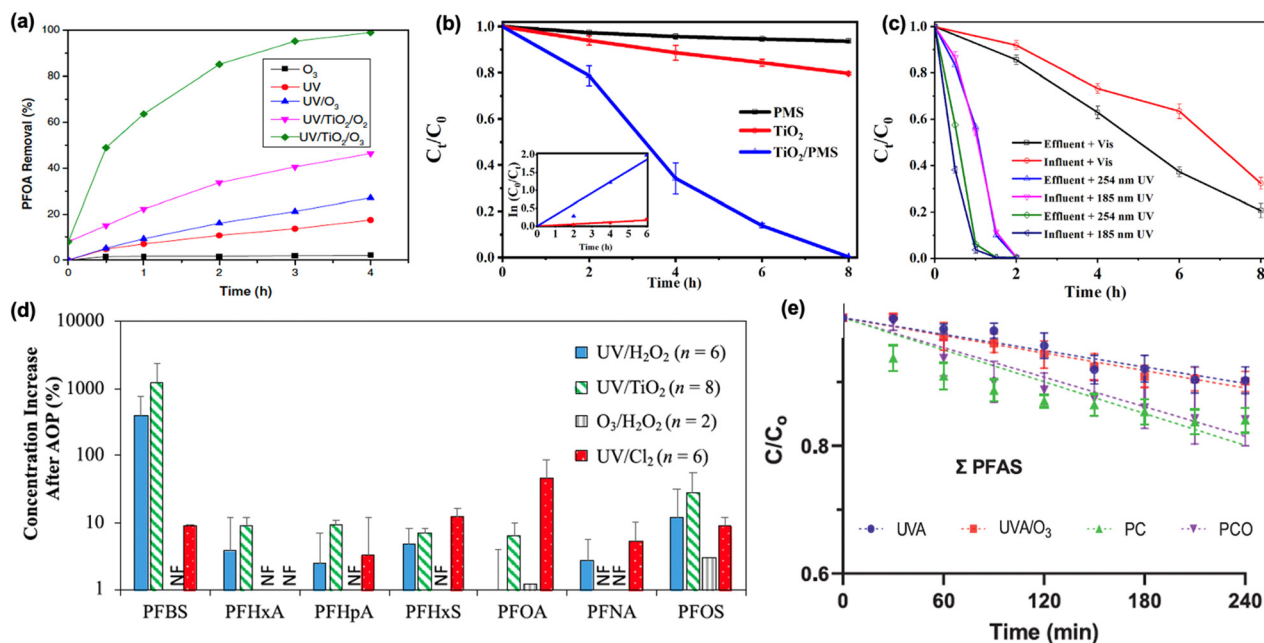


Fig. 16 (a) PFOA degradation and defluorination over 4 h under different treatments. Sole ozonation: 0.5% F defluorination; direct UV photolysis: 17.5% decomposition, 8.3% defluorination; TiO_2 photocatalysis ($\text{UV}/\text{TiO}_2/\text{O}_2$): 46.4% decomposition; UV/O_3 : 27.1% decomposition, 10.6% defluorination; photocatalytic ozonation ($\text{UV}/\text{TiO}_2/\text{O}_3$) achieved 99.1% decomposition and 44.3% C–F cleavage, highlighting strong synergistic effects. Reproduced from ref. 304 with permission from Elsevier BV, copyright 2016; photocatalytic degradation of PFOA (50 mg L^{-1}) using TiO_2/PMS : (b) under weak visible light (30 W) or darkness, PMS, TiO_2 , and TiO_2/PMS showed negligible removal. Under powerful visible light (300 W), TiO_2 alone removed $\sim 20\%$ of PFOA, PMS alone was ineffective, and TiO_2/PMS achieved nearly 100% degradation within 8 h, demonstrating a strong synergistic effect, (c) in real wastewater samples, TiO_2/PMS under 300 W visible light degraded 65–82% of PFOA within 8 h ($k = 0.136 \text{ h}^{-1}$ for influent, 0.070 h^{-1} for effluent), lower than that in pure water ($k = 0.310 \text{ h}^{-1}$) due to coexisting organics. UV light (254 and 185 nm) maintained degradation efficiency comparable to pure water, showing stable photocatalytic performance in complex matrices. Reproduced from ref. 305 with permission from Elsevier BV, copyright 2020; (d) fate of PFAS in pilot-scale AOP systems. Most targeted PFAS showed no significant removal, except PFHxA and PFHxS, which decreased by 7% and 11%, respectively, in the $\text{O}_3/\text{H}_2\text{O}_2$ effluent at Site 3. All other PFAS increased after treatment, with PFBS rising by 405% and PFOA/PFOS increasing by 14% and 13%, respectively. Variations between AOP technologies and sites reflect differences in precursor composition and source water quality. Reproduced from ref. 306 with permission from Elsevier BV, copyright 2022; (e) PFAS degradation after 4 h under different treatments. Photocatalysis and photocatalytic ozonation showed significantly higher removal of total PFASs, PFOA, PFHxS, and 6 : 2 FTS compared to photolysis ($p < 0.05$). Ozonation alone removed only $\sim 4\%$ and was not statistically different from adsorption. Reproduced from ref. 307 with permission from Elsevier BV, copyright 2022.

trace levels. To address these challenges, molecularly imprinted polymers (MIPs) have been employed for selective adsorption. For example, MIPs tailored for diclofenac achieved nearly 100% removal within 3 min at 5 mg L^{-1} , with high adsorption capacity (160 mg g^{-1}) and selectivity over structurally similar pharmaceuticals.³¹⁴ Hydrophilic MIPs synthesized *via* bulk polymerization removed $\sim 90\%$ of diclofenac in 10 min using only 5 mg of the material, compared to 8% removal by a non-imprinted polymer.³¹⁵ These studies demonstrate that molecular recognition-based materials can efficiently remove trace pollutants even in chemically complex environments.

Similarly, research has applied MIPs for selective PFAS removal. One strategy involves modifying TiO_2 nanotube arrays with MIPs, using PFAS molecules (*e.g.*, PFOA) as templates. The imprinted cavities selectively capture target PFAS near the TiO_2 surface, facilitating localized photocatalytic degradation.³¹⁶ Wu *et al.* demonstrated that MIP- TiO_2 nanotubes (MIP- TiO_2 NTs) selectively degrade PFOA in real secondary effluent. The material showed higher degradation efficiency for PFOA than that for PFHA, PFOS, or 2,4-dichlorophenoxyacetic acid (2,4-D), with apparent rate constants significantly greater for PFOA.

In secondary effluent (TOC 10.2 mg L^{-1} , pH 7.2), MIP- TiO_2 NTs achieved 81.1% PFOA removal in 8 h, comparable to 84% in pure water, whereas non-imprinted TiO_2 NTs reached only 50.2%. Furthermore, surface-molecularly imprinted TiO_2 nanotubes (S-MIP- TiO_2 NTs) was studied for enhanced photocatalytic degradation of PFAS in secondary municipal wastewater effluents.³¹⁷ S-MIP- TiO_2 NTs achieved significantly higher PFOA degradation under 8 h UV irradiation compared to TiO_2 NTs and non-imprinted controls, with defluorination efficiency markedly improved. Adsorption studies indicate selective binding driven by functional group recognition and electrostatic interactions at pH 4–6. Photocatalytic reactions follow Langmuir–Hinshelwood kinetics, resulting in rate constants exceeding those of non-molecularly imprinted polymer- TiO_2 NTs (NIP- TiO_2 NTs). This study demonstrated that S-MIP- TiO_2 NTs can selectively and efficiently degrade multiple short- and long-chain PFCs from real wastewater effluents at environmentally relevant concentrations. Complementing nanostructured MIP- TiO_2 systems, 3D-printed TiO_2 -poly(lactic acid) (PLA) composites were developed for pilot-scale PFAS treatment in landfill leachate.³¹⁸ Customized 3D-printed tiles containing 20 wt% TiO_2 achieved over 80% PFAS removal,



including PFOS, PFNA, PFDA, and PFOSAm, within 24 h, with even higher efficiency upon extended retention. This study highlighted the potential of additive manufacturing for creating scalable and efficient photocatalytic systems adaptable to real-world PFAS remediation.

7. Critical assessment of parameters, mechanisms, and modifications

Table 1 summarizes the comparative performance of TiO₂-based photocatalysts, including pristine, doped, composite, and immobilized systems, for PFAS degradation, highlighting key design strategies, degradation efficiencies, and operational stability. A critical comparative evaluation of these systems reveals clear performance hierarchies. Pristine TiO₂ (including P25) exhibits low degradation efficiency and defluorination (<30%), serving mainly as a benchmark.^{186,193,239} Noble-metal-modified TiO₂ (Pt-TiO₂) achieves complete PFOA degradation in 7 h with high kinetics (0.727 h⁻¹) and substantial defluorination (~35%).^{52,226} Heterojunctions such as BiOBr/TiO₂ provide high defluorination (~65%) and full degradation in 8 h.²³⁵ Carbon-supported hybrids (Fe/TNTs@AC) combine fast kinetics, high degradation (~90%), and excellent stability.^{255,259} Emerging MXene/TiO₂ systems show up to 94.6% degradation and ~58% defluorination, providing scalable, noble-metal-free alternatives.^{282,283} Photoelectrocatalytic TiO₂ systems achieve the highest overall performance (~99.5% degradation, 1.63 h⁻¹) though requiring applied bias and more complex reactors.^{296,297}

A comprehensive understanding of TiO₂-based PFAS photocatalysis necessitates the simultaneous evaluation of operational parameters, mechanistic pathways, and structural modifications (Fig. 17). These factors collectively determine degradation efficiency, selectivity, and stability. In this section, we critically assess the influence of key operational parameters, elucidate mechanistic insights into reactive species generation and C-F bond cleavage, and examine how structural and compositional modifications enhance charge separation and photocatalytic reactivity.

7.1. Influence of operational parameters

7.1.1. pH and surface charge effects. Photocatalytic performance of TiO₂-based photocatalysts in PFAS degradation is strongly governed by solution pH and the associated surface charge of the catalyst, which control PFAS adsorption, interfacial electron transfer, and reactive species generation. Acidic conditions favor degradation by protonating the catalyst surface, enhancing electrostatic attraction toward anionic PFAS molecules and promoting the formation of reactive species such as •OH and h⁺.^{185,186,196,198} At higher pH, surface deprotonation occurs, and OH⁻ ions compete with PFAS for adsorption, reducing surface interactions and limiting photocatalytic activity. This behavior is directly related to the point of zero charge (pH_{pzc}) of the catalyst, which defines the pH at which the surface has a net neutral charge. When the solution pH exceeds pH_{pzc}, the surface becomes negatively charged, decreasing the adsorption of anionic PFAS and hindering subsequent photocatalytic reactions.

To overcome these pH-dependent limitations, various surface modifications and composite strategies have been employed. In Fe/TNTs@AC composites, for instance, pH-related limitations are mitigated through surface modification.²⁵⁵ Pristine TNTs (pH_{pzc} = 2.57) show negligible PFOA adsorption due to their negative charge. Incorporation of Fe₂O₃ on TNT@AC raises pH_{pzc} from 3.8 to 5.2, reducing repulsion and enhancing anionic PFOA adsorption. α-Fe₂O₃ (pH_{pzc} = 6.7) attracts PFOA's carboxylate head (pK_a ≤ 3) *via* electrostatic and Lewis acid–base interactions, while AC supports hydrophobic and anion–π interactions with the perfluorinated tail. This cooperative adsorption aligns PFOA for efficient hole-driven decarboxylation at the α-Fe₂O₃/TNTs interface. The composite achieves ~99% PFOA adsorption (pH 4–11) and ~61% defluorination at pH 4–8, declining to 56.8%, 42.7%, and 36.1% at pH 9–11. Other TiO₂ composites show similar adaptability: Fe:Nb–TiO₂ maintains activity from pH 4.3 to 9 *via* Fe-induced bandgap narrowing and Nb-assisted charge separation,²²³ In/TNTs@AC supports hole-driven decarboxylation over pH 4–11,²⁵⁹ TiO₂–Pb/rGO sustains ROS-dominated degradation (h⁺, •O₂⁻, and ¹O₂) at pH 4.5–7.5²⁶⁷ and TiO₂-assisted photocatalytic ozonation achieves 99.1% PFOA removal and 44.3% defluorination under UV across pH 3–9.³⁰⁴ These advances extend TiO₂'s operational pH window, enhancing its practicality for PFAS remediation.

7.1.2. Catalyst loading and atmosphere. Catalyst dosage also plays a dual role: moderate TiO₂-based photocatalysis loadings optimize UV light absorption and active site availability, while excessive loading leads to light scattering and reduced photon penetration, resulting in decreased degradation efficiency.^{186,193,239} For example, in the Sb₂O₃/TiO₂ heterojunction system, an optimal 3 wt% Sb₂O₃ content achieved 81.8% PFOA degradation within 120 min, but higher catalyst concentrations suppressed activity due to agglomeration and recombination losses.²³⁹ The type of oxidizing atmosphere further dictates reaction kinetics, oxygen-rich conditions favor reactive oxygen species (ROS) formation, while N₂ atmospheres can enhance reductive degradation pathways involving CO₂^{•-} radicals, particularly in the presence of organic electron donors like oxalic acid.¹⁸⁸

7.1.3. Temperature and light effects. Temperature and light conditions introduce additional complexity. While TiO₂ typically operates efficiently at ambient temperature (~25–30 °C), elevated temperatures can increase reaction rates up to an optimal limit before desorption effects dominate.^{193,201} The wavelength and intensity of illumination directly affect photon utilization; UV-C (254 nm) irradiation remains the most effective for initiating C–F bond scission, yet visible-light-responsive systems, achieved through metal or nonmetal modification, are gaining attention.^{223,235,274} Temperature also influences charge carrier dynamics and radical generation. For instance, TiO₂/zeolite nanocomposites demonstrated enhanced PFOA degradation, where defluorination efficiency increased from 47.1% at 25 °C to 48.4% at 85 °C, with optimal performance below 100 °C to prevent thermal interference with photocatalytic pathways.²⁸⁴ Elevated temperature promoted •OH radical formation and accelerated surface oxidation by improving charge carrier mobility and reducing recombination losses. These findings demonstrate that





Material	PFAS studied	Amount of PC; amount of PFAS; solution volume	Light used	Rate constant	Degradation/removal; defluorination, time	Cycle	Ref.
Pristine TiO₂ photocatalysis							
TiO ₂	HFBA, TFA, PFPA, NFPA, PFOA, NFBS, HFOS	2 g L ⁻¹ ; 1.5–6 mM; 50 mL	UV light, 75 W, 1.4–7.2 mW cm ⁻²	0.0024–0.0123 h ⁻¹	CO ₂ : 12–54%, F ⁻ : 15–64%, 60 h	—	185
TiO ₂	PFOA, PFDA, PFNA	0.66 g L ⁻¹ ; 48–120 μM, with 0.15 M HClO ₄ ; —	UVC light, 16 W, 0.45 mW cm ⁻²	0.1–0.94 h ⁻¹	Decomposition: 86–100%, 7 h, mineralization: 30–54%, 7–48 h	—	186
TiO ₂ (commercial RdH; sol-gel, sonication-assisted)	PFOA (120 μM)	0.66 g L ⁻¹ ; 120 μM; 2 L (reactor)	UV light, 8–16 W	0.0342 h ⁻¹ (RdH), 0.1309 h ⁻¹ (sol-gel) with ultrasound	Degradation: 22%, 7 h (RdH); ~40%, 7 h sol-gel; ~64%, 8 h (sol-gel + ultrasound)	—	187
TiO ₂	PFOA + intermediates	0.5 g L ⁻¹ ; 24 μM; 500 mL	UV light, 23 W	1.16 × 10 ⁻² min ⁻¹	Degradation: 86.7%, 3 h; defluorination: 16.5%, 3 h	—	188
TiO ₂ (biosynthesized)	PFOS	—; 200 μg L ⁻¹ ; 50 mL	UV light	—	Degradation: 95.6%, 2.5 h; defluorination: 56.1%, 2.5 h	—	196
TiO ₂	PFOS	1.45 g L ⁻¹ ; 100 μg L ⁻¹ ; 100 mL	UV light, 250 W	0.64 h ⁻¹	Degradation: 86%, 8 h	—	198
TiO ₂	PFOA	0.66–1.0 g L ⁻¹ ; 0.0040–0.0120 M; 1 L	UV light, 500 W, 75–95 W m ⁻²	0.0332–0.0572 h ⁻¹	Mineralization: 32%, 4 h; F ⁻ : 29%, 6 h	—	193
TiO ₂	PFOA	1.5 wt%; 5 mM; 0.1 L	MPUV light, 600 mW cm ⁻²	—	Degradation: 8.6 × 10 ⁻² dm ³ h ⁻¹ , 4 h	—	200
TiO ₂	PFBA, PFHxA, PFOA, PFHxS, PFOS; precursors: 6:2/8:2 diPAP, 6:2/8:2 sFTSA, 6:2/8:2 FTCA, PFOA, N-EtFOSAA	430 mg L ⁻¹ ; 100 μg L ⁻¹ ; solution: 1 L	UV/TiO ₂ (PhotoTOP), Pyrex glass, ~60 °C, steady state	—	Degradation (of precursors): 100%, 2–4 h	—	201
TiO ₂	PFOA	0.5 g L ⁻¹ ; 60 mg L ⁻¹ ; 120 mL	UV light, 125 W, 5.3 mW cm ⁻²	0.058 h ⁻¹	Degradation: 31.1%, 7 h; defluorination: 3.3%, 7 h	—	226
TiO ₂ (mesoporous)	PFOA	0.25 g L ⁻¹ ; 10 ppm; 20 mL	UV light, 4 W	6.3 × 10 ⁻³ min ⁻¹	Degradation: 55.9%, 2 h	—	239
TiO ₂	PFOA	0.1–0.2 g L ⁻¹ ; 10 mg L ⁻¹	UV light, 30 W; Xe lamp, 300 W	—	Degradation: 15%, 4 h	—	235
TiO ₂	PFOA + intermediates	0.05–0.5 g L ⁻¹ ; 0.24 mmol L ⁻¹ ; 0.8 L	Mercury lamp 200–600 nm	—	Degradation: 24 ± 11%, 12 h	—	266
TiO ₂	PFHpA, PFHxA, PFPeA, PFBA	0.3 g L ⁻¹ ; 0.24 mmol L ⁻¹ ; 0.8 L	UV-A/B/C, visible, 150 W	0.018 h ⁻¹	Degradation: 10%; defluorination: 2%	—	268
TiO ₂	PFPA	0.5 g L ⁻¹ ; 10 mg L ⁻¹ ; solution: n/a	UV light, 8 h	—	TiO ₂ : 48.4% defluorination	—	284
TiO ₂	PFOA	0.33–0.66 g L ⁻¹ ; 10 mg L ⁻¹ ; 21 mL	UV light, 15 W	0.0068 h ⁻¹	—	—	267
UV/TiO ₂ pilot system	PFBS, PFHxA, PFHpA, PFHxS, PFOA, PFOS, PFNA	TiO ₂ slurry; PFAS 0.3–8.2 mg L ⁻¹ ; flow 26.5 L min ⁻¹	32 low-pressure UV lamps (7 kW)	Not reported	PFAS increase with UV power; ΣPFAS up to 103% at Site 2	1 Phase	306
Doped-TiO₂ systems							
Fe:Nb-TiO ₂	PFOA	0.5 g L ⁻¹ ; 0.1 mM; 600 mL	MP mercury lamp 150 W,	—	Stepwise degradation to shorter PFACs (C6, C5, and C4), fluoride ions released	—	223
Fe-TiO ₂	PFOA	0.5 g L ⁻¹ ; 50 mg L ⁻¹ ; 1 L	UV light, 400 W, 120 000 lux	0.0015 min ⁻¹	Degradation: 69%, 12 h; defluorination: 9%, 12 h	—	224
Cu-TiO ₂	PFOA	0.5 g L ⁻¹ ; 50 mg L ⁻¹ ; 1 L	UV light, 400 W, 120 000 lux	0.0031 min ⁻¹	Degradation: 91%, 12 h; defluorination: 19%, 12 h	—	224
Pt-TiO ₂	PFOA	0.5 g L ⁻¹ ; 60 mg L ⁻¹ ; 120 mL	UV light, 125 W, 5.3 mW cm ⁻²	0.7267 h ⁻¹	Degradation: 100%, 7 h; defluorination: 34.8%, 7 h	—	226
Pd-TiO ₂	PFOA	0.5 g L ⁻¹ ; 60 mg L ⁻¹ ; 120 mL	UV light, 125 W, 5.3 mW cm ⁻²	0.4369 h ⁻¹	Degradation: 94.2%, 7 h; defluorination: 25.9%, 7 h	—	226
Ag-TiO ₂	PFOA	0.5 g L ⁻¹ ; 60 mg L ⁻¹ ; 120 mL	UV light, 125 W, 5.3 mW cm ⁻²	0.1257 h ⁻¹	Degradation: 57.7%, 7 h; defluorination: 8.1%, 7 h	—	226

Table 1 (continued)

Material	PFAS studied	Amount of PC; amount of PFAS; solution volume	Light used	Rate constant	Degradation/removal; defluorination, time	Cycle	Ref.
Pb-TiO ₂	PFOA	0.5 g L ⁻¹ ; 50 mg L ⁻¹ ; 1.1 L (reactor)	UV light	0.5136 h ⁻¹	Degradation: 99.9%, 12 h; defluorination: 22.4%, <i>t</i> _{1/2} 1.3 h	—	229
TiO ₂ -Pb	PFOA	0.33–0.66 g L ⁻¹ ; 10 mg L ⁻¹ ; 21 mL	UV light, 15 W	0.0571 h ⁻¹	Removal: 80%, 24 h; defluorination: 12%, 24 h	—	267
Single-atom catalysis (SACs) on TiO₂					Significant	10 (Pt)	52
Facet-engineered TiO ₂ , PtNP/facet-engineered TiO ₂ , Pt1/facet-engineered TiO ₂	PFOA	0.25 g L ⁻¹ ; 100 μM; 80 mL	UV light, 5 W, 7.87 mW cm ⁻²	Negligible, NA, 15 × PtNP			
N/C1-Bi/TiO ₂ variants	PFOA	0.2 g L ⁻¹ ; 10 mg L ⁻¹ ; 100 mL	UV light, 30/300 W	—	Defluorination: 55–85%, 4 h	4	235
TiO₂ coupled with other semiconductors or oxides							
1–10%-Sb ₂ O ₃ /TiO ₂	PFOA	0.25 g L ⁻¹ ; 10 ppm; 20 mL	UV light, 4 W	12.6 × 10 ⁻³ min ⁻¹	Degradation: 10–81.8%, 2 h	5	239
P25/BiOBr	PFOA	0.5 g L ⁻¹ ; 100 mg L ⁻¹ ; 1 L	300 W, Xe lamp, 320–780 nm, 120 mW cm ⁻²	—	Degradation: 99.7%, 100 min; defluorination: 39.8%, 100 min	4	240
1–5% ReS ₂ -TiO ₂	PFOA, PFHXA, PFPeA, PFOS, PFDA, PFHpA	25 mg, 2 mg L ⁻¹	UV light	0.021–0.030 min ⁻¹	PFOA, degradation: 98%, 2 h; defluorination ~75%, 2 h	—	241
BN/TiO ₂	PFOA	0.5 g/L, 120 μM; 20 mL	365 nm UV-A, 254 nm UV-C, natural sunlight	<i>t</i> _{1/2} = 55 min (365 nm UV-A), <i>t</i> _{1/2} = 13 min (254 nm UV-C), <i>t</i> _{1/2} = 1.7 h (sunlight DI water), <i>t</i> _{1/2} = 4.5 h (sunlight model water)	Defluorination: 37% (365 nm, 4 h), >50% (254 nm, 1 h), 60% (sunlight, DI water, 4 h), 68% (sunlight, DI water, 7 h), 31% (sunlight, model water, 7 h)	4	36
Carbon-based hybrid photocatalysts							
TiO ₂ -MWCNT composites	PFOA	1.6 g L ⁻¹ ; 30 mg L ⁻¹ ; 250 mL	UV light, 300 W	—	Removal: 94–100%, 8 h	—	265
TiNTs@AC	PFOA	4.0 g L ⁻¹ ; 100 μg L ⁻¹ ; 10 mL	UV light, 21 mW cm ⁻²	—	Removal: 83.3%, 4 h; defluorination: 41%, 4 h;	—	255
Fe/TiNTs@AC	PFOA	4.0 g L ⁻¹ ; 100 μg L ⁻¹ ; 10 mL	UV light, 21 mW cm ⁻²	0.918 h ⁻¹	Removal: 91.3%, 4 h; defluorination: ~62%, 4 h	6	255
In/TiNTs@AC	PFOA	4 g L ⁻¹ ; 400 μg L ⁻¹ ; 10 mL	UV light, 2.28 mW cm ⁻²	—	Removal: 100%, 4 h; defluorination: 60%, 4 h	4	259
TiO ₂ -rGO (5 wt% rGO)	PFOA	0.1 g L ⁻¹ ; 0.24 mmol L ⁻¹ ; 0.8 L	UV-A/B/C, visible, 150 W	0.211 h ⁻¹	Removal: 86%, 8 h; defluorination: 30%, 8 h	—	268
TiO ₂ /rGO	PFOA	0.33–0.66 g L ⁻¹ ; 10 mg L ⁻¹ ; 21 mL	UV light, 15 W	0.0410 h ⁻¹	Removal: 70%, 24h; defluorination: 25%	—	267
TiO ₂ -Pb/rGO	PFOA	0.33–0.66 g L ⁻¹ ; 10 mg L ⁻¹ ; 21 mL	UV light, 15 W	0.2193 h ⁻¹	Removal: 98%, 24 h; defluorination: 32%, 24 h	—	267
3D SG-TiO ₂ QDa	PFOA,	4.8 mg/200 mL; 0.30 mmol L ⁻¹ ; 200 mL	UV light, 150 W	1.898 × 10 ⁻⁴ /s	—	—	272
3D SG-TiO ₂ QDb	PFOA	4.8 mg/200 mL; 0.30 mmol L ⁻¹ ; 200 mL	UV light	1.530 × 10 ⁻⁴ /s	—	—	272
3D SG-TiO ₂ NP	PFOA	4.8 mg/200 mL; 0.30 mmol L ⁻¹ ; 200 mL	UV light	9.283 × 10 ⁻⁵ /s	—	—	272
MCQD/TiO ₂	PFOA	0.1 g L ⁻¹ ; 100 μg L ⁻¹ ; 100 mL	UV light, visible light	—	UV: degradation: 29%; visible: degradation: 20%	—	273
Exfol.CQD/TiO ₂	PFOA	0.1 g L ⁻¹ ; 100 μg L ⁻¹ ; 100 mL	UV light, visible light	—	UV: degradation: 69%; defluorination: 34.5%; visible: degradation: 50%; defluorination: 32.0%	3	273



Table 1 (continued)

Material	PFAS studied	Amount of PC; amount of PFAS; solution volume	Light used	Rate constant	Degradation/removal; defluorination, time	Cycle	Ref.
Exfol.CQD/TiO ₂	PFHxA, PFPeA, PFBA, PFPrA	0.1 g L ⁻¹ ; 100 µg L ⁻¹ ; 100 mL	Visible light	—	PFHxA: degradation: 40%; PFPeA: degradation: 35%; PFBA: degradation: 31.6% PFPrA: degradation: 21.6% Defluorination: 56.2% (UV), 46.6% (visible) Defluorination: 10.9% (visible), 12.9% (UV)	—	273
PCQD/TiO ₂	PFOA	1 g L ⁻¹ ; 100 µg L ⁻¹ ; 100 mL	UV light, 4 × 16 W; visible light, 200 W	—	Defluorination: 56.2% (UV), 46.6% (visible)	3	274
PCQD/TiO ₂	Short-chain PFCAs (C3–C6)	1 g L ⁻¹ ; 100 µg L ⁻¹ each; 100 mL	UV light, 4 × 16 W; visible light, 200 W	—	Defluorination: 10.9% (visible), 12.9% (UV)	—	274
Emerging hybrid systems							
MXene/TiO ₂	PFOA	20 mg; 20–100 mg L ⁻¹ ; 150 mL	UV light	0.3296–0.1135 h ⁻¹	Removal: 62.97–94.64%; defluorination: 58.4%, 9 h	—	282
Ti ₃ C ₂ /TiO ₂ -80	PFOA	200 mg L ⁻¹ ; 20 µM	UV light, 20 mW cm ⁻²	—	Removal: > 99.9%, F ⁻ 49%, 16 h	4	283
Ti ₃ C ₂ -HF/TiO ₂	PFOA	200 mg L ⁻¹ ; 20 µM	UV light, 20 mW cm ⁻²	—	Removal: 22%, F ⁻ 12%, 16 h	—	283
TiO ₂ /zeolite	PFPA	0.5–1.0 g L ⁻¹ ; 10 mg L ⁻¹ ; 1 L	UV light, 16W	—	Removal: 54.5%, 8 h	—	284
F-TiO ₂ @MIL-125	PFOA, PFHpa, PFHxA, PFPeA	4 mg; 300 µmol L ⁻¹ (PFOA); 200 mL	Visible light	1.221 × 10 ⁻⁴ /s	PFOA: rapid decrease in the first 2 h.	7	66
Photoelectrocatalysis (PEC)							
GO/TNA	PFOA	5 × 5 cm ² ; 0.121–2.42 mM; 1.4 L	UV light, 8 W; UV light + external bias (0–2 V)	0.34 h ⁻¹ (25 °C, UV); 1.63 h ⁻¹ (75 °C, UV)	UV only: 83% in 4 h; PEC (2 V): 99.5%	3	295
TiO ₂ nanoporous (BEEP PFTeDA (C14), PFNA photoreactor)	(C9), PFOS, 42 PFAS mixture	TiO ₂ grown on inner Ti tubes; PFAS 100 ppm (single analyte)/42 PFAS mixture; 2 L solution	UVA 365 nm LED + 2 V bias (BEEP)	—	PFTeDA: below detection in 12 h; PFOS: ~15% defluorination in 24 h; 42 PFAS: longer chains fully degraded in 24 h; smaller chains formed	—	296
TiO ₂ photoanode (plasma electrolytic oxidation on Ti mesh; anatase 58%, rutile 42%)	PFOA, PFHpa, PFHxA, PFPeA, PFBA, PFOS, PFHps, PFHXS, PFBS	TiO ₂ mesh; PFOA 2 µg L ⁻¹ in ultra-pure water; groundwater: 873–1604 ng L ⁻¹ total PFAS; reactor volume 1 L	UV (two lamp powers, P1 and P2); photoelectrocatalysis (PEC)	PFOA: 0.00461–0.00652 min ⁻¹ (PEC P1); PFHpa: 0.00242–0.00428 min ⁻¹ ; PFHxA: 0.00142–0.00309 min ⁻¹ ; PFPeA: 0.00179–0.00315 min ⁻¹ ; PFBA: 0.00265–0.00292 min ⁻¹ ; PFOS: 0.00261 min ⁻¹ ; PFHps: 0.00134 min ⁻¹	PFOA 96%, PFHpa 73%, PFHxA 75%, PFPeA 69%, PFBA 77%, PFOS 68%, PFHps 40%, PFBS 1% @ 600 min	2	297
TiO₂ nanotube arrays (TNAs) with molecularly imprinted polymers (MIPs)							
S-MIP-TiO ₂ NTS, NIP-TiO ₂ NTS, TiO ₂ NTS	PFBA, PFPeA, PFHxA, PFHpa, PFOA	Active area: 400 cm ² L ⁻¹ ; 10–10 ⁹ ng L ⁻¹ ; Wastewater: 10 µg L ⁻¹ ; solution: 300 mL (adsorption)	UV light, 8 W	TiO ₂ NTS 0.0225, NIP-TiO ₂ NTS 0.0316, S-MIP-TiO ₂ NTS 0.0732 min ⁻¹	S-MIP-TiO ₂ NTS > NIP-TiO ₂ NTS > TiO ₂ NTS	5	317
TiO ₂ NTS, NIP-TiO ₂ NTS, MIP-TiO ₂ NTS	PFOA, PFHA, PFOS, MIP-TiO ₂ NTS	—; 50 µmol L ⁻¹ ; competitive: PFOA 50 µmol L ⁻¹ + other PFASs 25 µmol L ⁻¹ ; —	UV light	TiO ₂ NTS 0.0011, NIP-TiO ₂ NTS 0.0022, MIP-TiO ₂ NTS 0.0036 min ⁻¹	TiO ₂ NTS 41%, NIP-TiO ₂ NTS 67%, MIP-TiO ₂ NTS 84%; secondary effluent: UV 18%, NIP-TiO ₂ NTS 50.2%, MIP-TiO ₂ NTS 81.1%; F ⁻ release after 8 h: photolysis 5.4%, TiO ₂ NTS 9.7%, NIP-TiO ₂ NTS 15.7%, MIP-TiO ₂ NTS 30.2%; TOC removal by MIP-TiO ₂ NTS ~46%; —	—	316



Table 1 (continued)

Material	PFAS studied	Amount of PC; amount of PFAS; solution volume	Light used	Rate constant	Degradation/removal; defluorination, time	Cycle	Ref.
PLA/TiO ₂ composite tiles	PFOS, PFOA, PFHxA, PFBA, PFNA, PFDA, PFOSAm	14.7 wt% TiO ₂ ; 850 cm ² chamber surface; PFOS 130 ng L ⁻¹ , PFOA 1100–1500 ng L ⁻¹ , PFHxA 2900 ng L ⁻¹ , PFBA 2500 ng L ⁻¹ , PFNA 29 ng L ⁻¹ , PFDA 30 ng L ⁻¹ , PFOSAm 5.7 ng L ⁻¹ ; PFUnDA/PFOA near detection limit; —	UV light, ~0.34 W m ⁻² ; cumulative 0.086–0.129 MJ m ⁻²	—	Mass removal rates: PFOS 2962–3072 ng m ⁻² day ⁻¹ ; degradation: PFOS 91–95%, PFNA 89–93%, PFDA 86–95%, PFOSAm 89–92%, PFOA 39–78%; short-chain PFASs increased due to longer-chain degradation; HRT 24 h vs. 36 h; better removal at 36 h	—	318
Hybrid advanced oxidation processes (AOPs)							
TiO ₂ /O ₃	PFOA	0.2 g L ⁻¹ ; 10 mg L ⁻¹ ; 1 L	UV light, 28 W	—	Using O ₃ : 99.1% degradation, 44.3% C-F, 4 h	—	304
TiO ₂ /PMS	PFOA	0.25 g L ⁻¹ ; 50 mg L ⁻¹ ; 200 mL	300 W, 400–770 nm	0.310 h ⁻¹	100%, 8 h	—	305
TiO ₂ /PMS	PFOA	0.25 g L ⁻¹ ; 50 mg L ⁻¹ ; 200 mL	32 W, 254 nm	1.09 h ⁻¹	98%, 1.5 h	—	305

fine-tuning operational parameters is crucial for balancing adsorption, photon flux, and charge transfer dynamics in TiO₂-driven PFAS degradation systems.

7.2. Mechanistic insights

A commonly proposed degradation pathway for PFOA begins with photoinduced oxidative decarboxylation, producing perfluoroalkyl radicals ($\cdot\text{C}_n\text{F}_{2n+1}$). These radicals then undergo reactions with O₂ or H₂O to form perfluoroalcohol intermediates, which subsequently yield shorter-chain PFCAs through β -scission and hydrolysis. The chain-shortening continues stepwise until CO₂ and F⁻ are released. This mechanism has been supported by LC-MS and ion chromatography analyses, revealing time-dependent decreases in PFOA and corresponding increases in fluoride ions.^{186,188,239}

While oxidative routes dominate under oxygen-rich conditions, reductive pathways have also been recognized as critical for effective defluorination, especially under UV irradiation in the presence of organic hole scavengers (*e.g.*, methanol or oxalic acid). The conduction band electrons in TiO₂ can react with O₂ to form O₂^{•-} or directly attack the carbon-fluorine bonds *via* hydrated electrons (e_{aq}⁻) or CO₂^{•-} intermediates, enabling partial reduction of highly stable PFAS.¹⁸⁸ This dual-pathway mechanism, where oxidative and reductive routes operate concurrently, explains why systems with balanced oxygen availability and sacrificial donors often exhibit superior degradation rates compared to purely oxidative setups.⁵²

Moreover, the crystal phase and exposed facets of TiO₂ critically influence charge separation and ROS generation. Anatase TiO₂ typically exhibits superior photocatalytic activity compared to rutile, owing to its higher surface area and lower e⁻-h⁺ recombination rates.^{37,52,223} Surface modifications, such as fluorination or oxygen vacancies (TiO_{2-x}), further enhance electron trapping and extend carrier lifetimes, promoting $\cdot\text{OH}$ radical formation and effective C-F bond cleavage.^{235,274} Incorporation of carbon-based materials, including graphene oxide or MWCNTs, improves electron conductivity and facilitates π - π interactions with PFAS molecules, enhancing charge transfer and radical-mediated degradation.²⁶⁵

The reaction kinetics of PFAS degradation generally follow a pseudo-first-order model, highlighting the importance of electron transfer between TiO₂ and adsorbed PFAS molecules. Degradation rates can be influenced by PFAS' chain length, surface adsorption, and operational conditions such as pH, dissolved oxygen, light intensity, temperature, and the presence of co-contaminants. Short-chain PFAS may degrade more slowly due to weaker adsorption, whereas long-chain PFAS, despite stronger initial adsorption, often undergo slower complete mineralization. These insights underscore the need to optimize both the interplay of surface adsorption and e⁻-h⁺ utilization and the operational parameters to achieve efficient defluorination and total organic carbon removal in TiO₂-based PFAS remediation systems.

7.3. Structural and compositional modifications

7.3.1. Bandgap engineering *via* doping and decoration.

Transition-metal doping and noble-metal decoration have two recurring effects: narrowing the optical bandgap or introducing



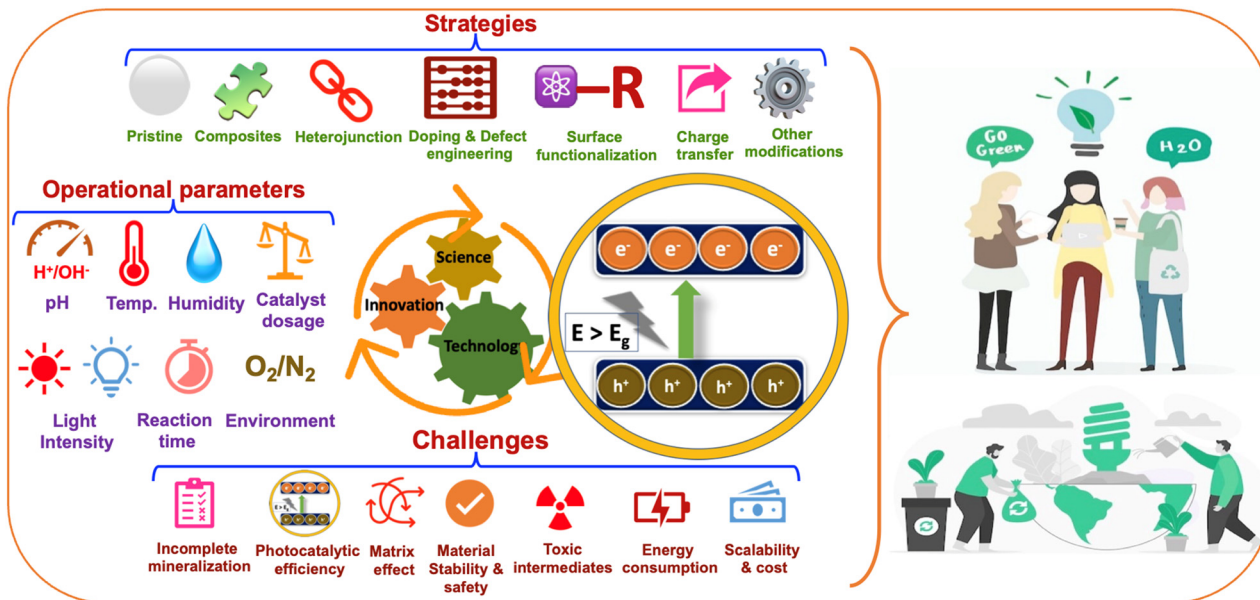


Fig. 17 Overview of strategies, operational parameters, and remaining challenges involved in TiO_2 -based photocatalysis. Note: some elements of this figure are adapted from graphics designed by Freepik (rawpixel.com/ Freepik, <https://www.freepik.com/>) and Pixabay (<https://pixabay.com/>), used in accordance with their licenses.

midgap states that extend light absorption toward visible wavelengths and acting as electron traps that reduce recombination. Cu- and Fe-doped TiO_2 systems outperformed bare TiO_2 in PFOA decomposition, with Cu doping particularly effective at lowering the bandgap and enhancing e^- trapping.²²⁴ Noble metals (Pt, Pd, and Ag) act as efficient electron sinks and promote hole-driven oxidation; the ordering $\text{Pt} > \text{Pd} > \text{Ag} > \text{TiO}_2$ observed in one comparative study evidences the benefit of strong electron trapping and Schottky junction formation for enhanced h_{vb}^+ activity and intermediate PFCA formation (PFHpA-PFPrA) leading toward $\text{CO}_2 + \text{F}^-$.²²⁶ Most striking mechanistic advances come from single-atom catalysts: facet-engineered TiO_2 with atomically dispersed Pt (Pt_1) not only improved charge separation but uniquely enabled both oxidative ($\bullet\text{OH}$ generation) and reductive (H spillover and hydrodefluorination) routes; the study reported substantial Ti-F surface binding ($\approx 58\%$ of fluorine associated with Ti-F), underscoring strong surface-mediated defluorination and single-atom stability *via* Pt-O coordination.⁵² These single-atom platforms therefore broaden the mechanistic toolkit from purely oxidative chain-shortening toward hybrid oxidative-reductive defluorination, an important step for challenging C-F bond cleavage.

7.3.2. Heterojunctions for enhanced photocatalysis. Creating intimate interfaces between TiO_2 and other semiconductors (BiOBr , ReS_2 , BN , Sb_2O_3 , *etc.*) enhances spatial charge separation and tailors the dominant ROS. S-scheme heterostructures such as ReS_2 - TiO_2 introduce an internal electric field and oxygen vacancies that selectively retain high-energy electrons and holes at appropriate sites, thereby increasing $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ formation and producing measurable gains in PFAS degradation over bare TiO_2 .²⁴¹ Sb_2O_3 loading is another demonstrable

success: an optimized 3 wt% $\text{Sb}_2\text{O}_3/\text{TiO}_2$ composition achieved $\sim 81.8\%$ PFOA degradation in 120 min with good reusability ($\sim 88\%$ retained after five cycles), while excessive loadings were detrimental due to light attenuation and recombination, illustrating the criticality of tuning interfacial content to balance light harvesting and charge dynamics.²³⁹

7.3.3. Conductive carbon supports for enhanced PFAS photocatalysis. Incorporation of conductive carbon supports, rGO, MWCNTs, CQDs, and graphene oxide fulfills multiple roles: electron conductivity to prolong charge carrier lifetimes, light absorption extension, and in some cases adsorption enhancement that localizes PFAS near reactive sites. Quantitatively, rGO decoration reduced the TiO_2 bandgap from 3.25 to 2.94 eV and improved photocatalytic performance, while MWCNT/ TiO_2 composites with an optimal 10 : 1 ratio combined adsorption with efficient electron storage to suppress recombination and drive stepwise CF_2 cleavage.^{265,266,268} Exfoliated CQD/ TiO_2 composites demonstrated markedly superior PFOA degradation (69% under UVC, 50% under visible) compared to bare TiO_2 (41%/24%), linking improved interparticle electron transfer and reduced aggregation to measurable gains in both conversion and defluorination stability.²⁷³ These results collectively show that conductive carbon frameworks are among the most practical routes to visible-light activity and suppressed recombination without relying solely on scarce noble metals.

7.3.4. Adsorptive and 2D supports for PFAS photocatalysis. Adsorptive enrichment increases local PFAS concentration at photocatalytic sites and can convert dilute, hard-to-treat streams into effectively treatable loads. Fe/TNTs@AC and In/TNTs@AC exemplify this strategy: low Fe loadings (~ 1 wt%) on TNTs@AC



enabled robust adsorption followed by h^+ -dominated Kolbe-like decarboxylation, producing stepwise C–F cleavage with reduced energy consumption compared to bulk aqueous approaches.^{255,259} Zeolite supports with TiO_2 achieved 54.5% defluorination at 85 °C and pH 13 (0.5 g L⁻¹ catalyst), highlighting that support choice and operating pH are decisive for defluorination yields.²⁸⁴ Molecularly imprinted polymer coatings (MIP- TiO_2 NTs) provide an additional level of selectivity for low-concentration PFAS in complex matrices, improving capture and subsequent photocatalytic turnover though attention must be paid to the risk of concentrating toxic intermediates if mineralization is incomplete.^{316,317} MXene/ TiO_2 composites (Ti_3C_2/TiO_2) and related 2D supports have emerged as powerful synergies of adsorption and electron transport. Intercalation strategies (*e.g.*, DES-assisted $NaBF_4$ intercalation) enlarge MXene spacing to favor TiO_2 growth and intimate contact, producing composites that outperform P25 in adsorption/photocatalysis and that display stable, reusable behavior (optimal $NaBF_4$ ~80 mM; pzc ≈ 5.8).²⁸³ MXene-based composites often report the active species order $\bullet OH > \bullet O_2^- > h^+$ and optimal pH values around 5.2, but like other high-adsorption supports they must be carefully dosed to avoid aggregation and UV scattering.^{282,283}

7.3.5. Reactor and hybrid process engineering. Beyond materials chemistry, reactor innovation (PEC, applied bias, photoelectrocatalytic meshes, and 3D-printed TiO_2 tiles) materially affects scalability and energy efficiency. Applied bias in nanoporous arrays (BEEP technology) enhanced charge separation sufficiently to operate across salinity ranges (0–35 g L⁻¹) and to preferentially degrade longer-chain PFAS first, generating short-chain intermediates that can then be further treated in downstream units.²⁹⁶ Photoelectrocatalytic treatment of groundwater in Veneto achieved ~63–65% removal across mixed PFAS compounds with lower energy input than photolysis at higher lamp power, illustrating that process integration (PEC *vs.* PL) can lower EEO while maintaining comparable efficacy.²⁹⁷ Hybrid oxidant strategies coupling TiO_2 with PMS or O_3 represent another practical path: TiO_2 /PMS delivered 100% PFOA removal under 300 W visible light (0.25/0.75 g L⁻¹ TiO_2 /PMS at pH 3) and UV/ TiO_2 / O_3 reached 99.1% degradation with 44.3% defluorination under acidic conditions, highlighting that the radical type ($SO_4^{\bullet-}$ *vs.* $\bullet OH$) and oxidant dosing strategy critically determine both conversion and defluorination efficacy.^{304,305}

8. Challenges and knowledge gaps

Despite the remarkable progress summarized above, the practical application of TiO_2 -based photocatalytic systems for PFAS degradation remains constrained by a combination of scientific, engineering, and environmental challenges (Fig. 17). These challenges extend beyond catalytic activity alone and encompass incomplete mineralization, energy efficiency, reactor scalability, matrix effects, catalyst stability, and mechanistic uncertainty. Addressing these interconnected limitations is essential for translating laboratory-scale successes into viable treatment technologies.

8.1. Incomplete mineralization and transformation limitations

The foremost limitation of TiO_2 -based PFAS photocatalysis is incomplete mineralization, even when high apparent degradation efficiencies are reported. In many systems, the disappearance of parent PFAS compounds does not correspond to full defluorination or conversion to CO_2 and inorganic fluoride. Instead, short-chain perfluorinated intermediates, particularly C₂–C₅ perfluorocarboxylates, tend to accumulate, some of which are equally or more recalcitrant and mobile than their long-chain precursors.^{186,304} This behavior arises from the exceptionally high C–F bond dissociation energy and the reduced adsorption affinity of short-chain PFAS toward TiO_2 surfaces. Consequently, extended irradiation times or secondary treatment stages are often required, underscoring that achieving selective and complete defluorination, rather than partial molecular transformation, remains a central mechanistic and catalyst-design challenge.

8.2. Material stability and environmental safety

Material stability and environmental safety represent critical challenges for the practical deployment of modified TiO_2 photocatalysts. Under prolonged irradiation, surface processes such as Ti–F bond accumulation can occur, leading to active-site passivation and suppression of further photocatalytic reactions. In parallel, leaching of dopant metals (*e.g.*, Cu, Fe, Sb, and Pb) or the release of nanoscale catalyst fragments during operation poses risks of secondary contamination and long-term performance deterioration.^{239,283} Although several modified TiO_2 systems exhibit acceptable recyclability over five to ten laboratory cycles with minimal activity loss, extended aging, fouling, mechanical integrity, and durability under realistic continuous-flow conditions remain largely uncharacterized. Beyond catalytic performance, comprehensive evaluation of toxicity and environmental compatibility is essential prior to large-scale implementation. Modified TiO_2 systems must be assessed for the formation of potentially harmful transformation by-products, metal ion release, and long-term ecological impacts under realistic water treatment conditions. Life-cycle considerations, including material synthesis, operational stability, and end-of-life disposal, remain largely overlooked in current photocatalysis studies but are critical for ensuring sustainable deployment.

Emerging composite materials further complicate stability and safety considerations. For example, MXene- TiO_2 hybrids are susceptible to surface oxidation and structural degradation in aqueous and oxidative environments,³¹⁹ particularly under prolonged illumination and in the presence of dissolved oxygen. Such degradation can reduce electrical conductivity, disrupt interfacial charge transfer, impair photocatalytic efficiency, and increase the likelihood of metal species release. Consequently, systematic long-term stability, leaching, toxicity, and environmental impact assessments under realistic operational conditions are required before modified TiO_2 catalysts, especially advanced composite systems, can be considered viable for sustained PFAS remediation.

8.3. Water matrix effects and process complexity

Matrix effects represent a significant challenge for the real-world application of photocatalytic systems. Constituents



commonly present in natural and wastewater matrices, such as bicarbonates, chlorides, natural organic matter (NOM), and competing inorganic anions, can substantially suppress photocatalytic activity by scavenging ROS or occupying active surface sites.^{320,321} Suspended solids, colored components, natural antioxidants, and mixed pollutants in real water matrices can further reduce photon penetration and pollutant-catalyst contact, exacerbating activity losses relative to idealized laboratory conditions. Beyond reducing degradation rates, these matrix components can alter reaction pathways and shift product distributions. Laboratory experiments conducted under idealized aqueous conditions often overestimate performance compared to complex environmental matrices. Dissolved oxygen (DO) is a critical chemical factor that interacts with water matrix effects. DO can enhance PFAS degradation in systems dominated by holes (h^+) by suppressing electron-hole recombination and promoting hydroxyl radical formation. Conversely, in systems where electron-mediated or direct photolysis pathways are dominant, high DO can suppress degradation efficiency. Matrix components and DO together influence real-water photocatalytic performance, affecting both reaction rates and pathways. Therefore, standardized testing protocols that incorporate realistic water chemistry, including DO levels, are essential for meaningful cross-study comparisons and scalable reactor design.

8.4. Energy efficiency and practical considerations

The energy required for PFAS photocatalytic degradation is a critical factor in evaluating the feasibility of treatment technologies.¹²⁵ Photocatalytic systems relying on UV-C irradiation or high-intensity mercury lamps may exhibit high electrical energy per order (EE/O) values when photon utilization is inefficient, potentially limiting large-scale implementation unless reactor design and irradiance are carefully optimized.³²² Despite its importance, EE/O is not reported consistently across studies, complicating direct techno-economic comparisons. Some studies have considered energy consumption metrics to evaluate and compare system performance. For example, BN/TiO₂ composites have been reported to achieve lower EE/O values than bare TiO₂, with lamp output-based EE/O values of $\sim 102 \text{ kWh m}^{-3} \text{ order}^{-1}$ under 254-nm irradiation and $\sim 253 \text{ kWh m}^{-3} \text{ order}^{-1}$ under 365-nm irradiation.³⁷ A TiO₂-Pb/rGO system achieved 98% PFOA removal with an EE/O of 4.05 kWh m^{-3} .²⁶⁷ PEC generally requires lower energy than PL, with EEO ranges of $20\text{--}150 \text{ kWh m}^{-3}$ (PEC) and $60\text{--}240 \text{ kWh m}^{-3}$ (PL).²⁹⁷ In ultrapure water, PEC EEO values for PFOA ($35.8\text{--}62.6 \text{ kWh m}^{-3}$) are much lower than sonolysis and photochemical oxidation and comparable to plasma and advanced reduction processes. Higher energy demand in groundwater is due to matrix complexity and lower PFAS concentrations.

8.5. Hybrid photocatalytic systems and operational complexity

Hybrid photocatalytic systems, including TiO₂/PMS and TiO₂/O₃, have been widely investigated for the enhanced degradation of persistent pollutants by combining direct photocatalytic oxidation with radical-mediated pathways.^{323,324} Although

these systems often outperform standalone photocatalysis under laboratory conditions, their practical implementation remains constrained by chemical complexity and operational limitations. A major challenge is the formation of undesirable transformation products. The generation of ROS (e.g., $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$) can promote rapid pollutant degradation, but competing side reactions are common in real water matrices.³²⁵ In the presence of nitrate or nitrite, reactive nitrogen species may form and induce nitration reactions, leading to nitrogen-containing by-products that can be more persistent and toxic than the parent compounds. As a result, high removal efficiencies do not necessarily correspond to reduced environmental risk, highlighting the importance of transformation product analysis and toxicity evaluation alongside conventional performance metrics.

Scalability is further limited by operational complexity. Hybrid systems depend on external oxidants such as persulfate, ozone, or hydrogen peroxide, which increase energy consumption, chemical usage, and process cost. Precise control of oxidant dosing and reaction conditions is required to avoid inefficiencies, secondary reactions, or residual oxidant release. Alternative hybrid configurations, such as photocatalysis combined with adsorption, membrane processes, or photoelectrocatalysis, can improve specific aspects of performance but introduce additional challenges related to reactor design, mass transfer, fouling, and material stability.^{326,327}

8.6. Engineering challenges and scalability considerations

TiO₂-based photocatalysis for PFAS degradation is still largely at the laboratory research stage, with most studies conducted under controlled ideal conditions. While these studies demonstrate the significant potential for photocatalysts, translating laboratory-scale findings into continuous-flow or field applications faces multiple engineering, operational, and scalability challenges.

8.6.1. Photocatalyst immobilization and stability. Immobilization remains a major bottleneck. Suspended or slurry-phase photocatalysts offer high surface areas but complicate separation, recovery, reuse, and containment.^{322,328} Immobilized configurations, including porous coatings, supported membranes, structured reactors, and 3D-printed monoliths, enhance retention, operational safety, and continuous-flow capability while minimizing secondary contamination. However, long-term stability under prolonged irradiation and in complex water matrices remains poorly understood. Immobilization can introduce mass-transfer limitations and reduced active-site accessibility, while activity losses may arise from surface deactivation, fluoride accumulation, photocorrosion, dopant leaching, or adsorption of intermediates. Prolonged operation may induce surface restructuring and active-site passivation, contributing to gradual performance decline.

8.6.2. Flow reactor design and mass transfer. Most lab studies employ batch reactors, which do not replicate continuous-flow conditions.^{329,330} Scaling up requires optimization of hydrodynamics, residence time, photon delivery, and pollutant-catalyst contact. Optical non-uniformities and mass-transfer limitations may arise upon scale-up.³²² Hybridized systems combining



membranes, cross-flow configurations, or adsorption-photo-catalysis approaches can mitigate fouling, enhance catalyst utilization, and improve operational flexibility.

8.6.3. LED and solar-assisted light sources. Light-emitting diode (LED)- and solar-assisted systems offer improved energy efficiency, wavelength tunability, and operational safety.³³¹ Limited light penetration and non-uniform photon distribution remain critical, especially in large-volume or continuous-flow reactors. UV reactors often rely on mercury-vapor lamps, with associated environmental issues, whereas visible-light-active composites enable LED use, though fabrication still involves rare earth elements.³³² Strategies to improve photon distribution include use of optimized LED arrays, reflective optics, and thin-film or immobilized catalysts, and solar-assisted hybrid operation.

9. Conclusions and perspectives

TiO₂-based photocatalysis has emerged as a versatile and promising strategy for PFAS remediation, offering sustainable pathways to break the highly resilient C–F bond. Advances in material modification, heterojunction engineering, and integration with conductive or carbonaceous supports have enhanced charge separation, light harvesting, and reactive species generation, leading to significant progress in PFAS degradation and establishing TiO₂-based systems as a leading and well-studied photocatalytic platform for PFAS treatment. In summary, this review not only highlighted recent advances in TiO₂-based photocatalysis for PFAS remediation but also critically assessed the influence of operational parameters, mechanistic pathways, structural and compositional modifications, hybrid and system-level strategies, and associated engineering and environmental challenges, providing a comprehensive overview of opportunities and remaining mechanistic gaps.

Looking forward, future research should prioritize hybrid and system-level strategies to improve efficiency and scalability. Photoelectrocatalytic configurations under low external biases can enhance charge separation, improve defluorination, and reduce energy consumption; coupling TiO₂ with conductive or tailored carbon materials such as graphene, carbon nitride, or MXenes can facilitate interfacial charge transport, lower overpotentials, and improve catalyst stability; and S-scheme heterojunctions help maintain strong redox potentials and suppress charge recombination. Integrated “concentrate-and-destroy” approaches, where TiO₂-coated adsorbents capture PFAS from dilute streams followed by *in situ* photodegradation, may overcome mass-transfer limitations and minimize secondary waste. To bridge laboratory innovation with field-scale applications, future efforts must emphasize environmental compatibility, sustainability, and safety, with rigorous evaluation of catalyst toxicity, transformation byproducts, and life-cycle impacts, combined with durable, scalable reactor designs and energy-efficient operation. Coordinated advances across materials science, process engineering, and policy frameworks, guided by molecular design principles and data-driven discovery, can transform TiO₂-based photocatalysis from a promising

research platform into a field-ready solution for one of today's most persistent forever chemicals.

Author contributions

Avtar Singh: conceptualization, investigation, methodology, visualization, writing – original draft, writing – review and editing, supervision; Thiagarajan Soundappan: writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included, and no new data were generated or analyzed as part of this review.

Acknowledgements

The authors express their gratitude to Dr Yogesh Singla, Navajo Technical University (NTU), NM, USA, alongside their other collaborators and peers for their invaluable insights in shaping this manuscript. The authors also extend their appreciation to the publishers for granting permission to reproduce figures used in this publication.

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