



Bioinspired hierarchical electrospun TiO₂/BiOI nanofibers for multifunctional photocatalytic PMS activation: Antibiotics and microplastics removal

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ABSTRACT

Emerging antibiotics and microplastics are poorly removed by conventional treatment processes, requiring oxidation processes that address both dissolved and particulate contaminants. Hierarchical electrospun TiO₂/BiOI nanofibers (TBO1–TBO4; BiOI growth 2–16 h) were engineered for photocatalytic peroxymonosulfate (PMS) activation under UV-A (365 nm) and visible light. At pH 7 and 20 °C (sulfamethoxazole, SMX, 5 ppm; catalyst 0.50 g L⁻¹; PMS 2.5 mM), TBO3 achieved near-complete, blank-corrected total organic carbon (TOC) removal (≥99%) in 120 min under visible light + PMS. For a four-component multipollutant solution (20 ppm total), TBO3 reached near-complete TOC removal after blank correction (reported as ≥99%, with residual TOC close to the method quantification limit) in 120 min and maintained activity over nine cycles under visible light + PMS (≤0.7 %age-point change; leaching below detection), whereas UV-A + PMS decreased to 85.3% by cycle 9 with ppb-level leaching. Quenching and probe assays indicate a radical-accessible PMS-assisted oxidation network; strong suppression by tert-butanol and methanol supports major [•]OH-accessible oxidation with a sulfate-radical-type contribution. Under visible light (465–470 nm) + PMS, cross-linked polystyrene (PS) microplastics (20 ppm solids) underwent surface erosion, cracking, delamination, and fragmentation, accompanied by release of dissolved/sub-10 μm carbonaceous products in scaled-up tests, supporting partial oxidative transformation of particulate microplastics.

1. Introduction

Water pollution remains a persistent environmental and public-health challenge because aquatic systems continuously receive complex mixtures of contaminants from domestic, agricultural, and industrial activities [1]. Among emerging pollutants, antibiotics and microplastics raise particular concern due to their persistence, broad distribution, and potential to affect both ecosystems and human health [2,3]. Antibiotics such as sulfamethoxazole (SMX) are frequently detected in wastewater effluents and surface waters at low concentrations, where conventional treatment trains can struggle to achieve complete removal [4,5]. Beyond their direct effects, residual antibiotics

contribute to the selection and spread of antibiotic-resistant bacteria, a major health risk [6]. In parallel, microplastics (i.e., plastic particles smaller than 5 mm) originate from the fragmentation of larger plastics and from urban or industrial sources such as synthetic textiles. These particles can be ingested by aquatic organisms and transferred along food chains, creating additional exposure pathways and complicating risk management in water reuse and receiving waters [7,8].

Traditional water treatment technologies, including physical separation and biological processes, are often insufficient for these contaminants because microplastics exhibit high physicochemical stability and many antibiotics show limited biodegradability [9]. This motivates advanced treatment approaches that can transform persistent organics

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and mitigate particulate pollutants using scalable and environmentally compatible chemistries [10–14]. Advanced oxidation processes (AOPs) address this need by generating reactive oxygen species (ROS) capable of oxidizing a broad range of organic pollutants, with the ultimate objective of extensive oxidation and, in favorable cases, mineralization to carbon dioxide, water, and inorganic ions [15–17]. Among AOPs, heterogeneous photocatalysis has attracted sustained interest because semiconductor catalysts can use light to generate oxidative and reductive equivalents under mild conditions, while avoiding the continuous dosing of stoichiometric oxidants [8,18,19].

Photocatalysis relies on photoexcitation of a semiconductor to form electron–hole pairs. Upon irradiation, electrons are promoted from the valence band (VB) to the conduction band (CB), leaving holes that can participate in interfacial redox steps. When charge carriers reach the surface before recombination, they can react with adsorbed species and dissolved oxygen to produce ROS such as hydroxyl radicals ($\cdot\text{OH}$) and superoxide radicals ($\text{O}_2^{\cdot-}$), which then oxidize organic matter [20,21]. A complementary strategy to intensify photocatalytic oxidation is the addition of peroxymonosulfate (PMS), which can be activated in photocatalytic systems to generate sulfate radicals ($\text{SO}_4^{\cdot-}$) [22–25]. The concurrent formation of $\text{SO}_4^{\cdot-}$ and other ROS expands the oxidative landscape and provides multiple reaction pathways for persistent contaminants, including antibiotics and microplastics [26,27]. Coupling photocatalysis with PMS activation therefore offers an additional route to intensify oxidative reactions while targeting a higher extent of pollutant transformation under practical operating conditions [28,29].

Catalyst design is central to efficient photocatalytic PMS activation in realistic water matrices [7,23,30]. Titanium dioxide (TiO_2 , anatase) is widely used due to its chemical stability, low toxicity, and low cost; however, its wide band gap (≈ 3.2 eV) confines light harvesting largely to the ultraviolet (UV) region, and rapid electron–hole recombination can limit performance [31,32]. Architecture control and semiconductor coupling are therefore used to increase accessible surface area, improve light utilization, and promote charge separation [33–36]. In this context, bioinspired hierarchical fibrous scaffolds offer more than high surface area: their multi-length-scale porosity and interconnected fiber networks can increase optical path length through multiple scattering, improving light utilization while simultaneously providing filtration-like transport pathways and abundant interfacial sites [37,38]. Here, electrospinning is used to fabricate TiO_2 -based nanofibers assembled into porous mats; importantly, electrospinning is compatible with continuous processing, supporting scale-up toward large-area, recoverable catalyst mats while preserving nanoscale control over morphology [21,39,40]. To extend absorption into the visible region and tune interfacial charge transfer, bismuth oxyiodide (BiOI) is integrated with TiO_2 [28,41,42]. BiOI is a p-type semiconductor with a narrow band gap (~ 1.8 eV), enabling visible-light absorption, and it is commonly considered biocompatible and non-toxic, attributes advantageous for environmental applications [29,43–46]. When combined with TiO_2 , BiOI can facilitate charge migration and support reactive oxygen species generation during PMS-assisted photocatalysis [28,41,42].

Despite progress in photocatalysis and PMS-based AOPs, the combined treatment of co-occurring antibiotics and microplastics within a single photocatalytic PMS-activation platform has received limited attention, and the scarcity of recoverable catalyst architectures complicates implementation beyond slurry reactors. Catalyst designs that simultaneously provide high interfacial area, effective light utilization, and practical mass transport are also less common, particularly when fabrication must be compatible with scale-up [31,47,48]. Here, bioinspired hierarchical electrospun TiO_2/BiOI nanofiber mats are introduced as a multifunctional catalyst format that integrates a porous fibrous scaffold in a free-standing geometry suited to handling and separation [35,49]. The material is evaluated for PMS-assisted photocatalytic water decontamination using SMX as a representative antibiotic, multipollutant solutions, and microplastics as a co-occurring

particulate pollutant, with the fibrous network designed to support interfacial reactions while facilitating transport and catalyst recovery [5,21,39]. This study links catalyst architecture and composition to mixed-contaminant treatment requirements, providing a single-process route that couples oxidative transformation of dissolved organics with mitigation of particulate pollutants.

2. Experimental section

2.1. Materials

Polyvinylpyrrolidone (PVP, $M_w \approx 1300,000$; Sigma-Aldrich; CAS 9003–39–8), ethanol (EtOH, 96% v/v; VWR Chemicals; CAS 64–17–5), titanium(IV) isopropoxide (TTIP, 97%; Sigma-Aldrich; CAS 546–68–9), and acetic acid (AA, 99–100%; VWR Chemicals; CAS 64–19–7) were used for electrospinning precursor solutions. For BiOI growth, bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$, $\geq 98\%$; Sigma-Aldrich; CAS 10035–06–0) and potassium iodide (KI, $\geq 99\%$; Panreac; CAS 7681–11–0) were used with ethylene glycol (EG, 99.8%; Sigma-Aldrich; CAS 107–21–1). Sulfamethoxazole (SMX; Sigma-Aldrich; CAS 723–46–6), tetracycline (TC; Alfa Aesar; CAS 60–54–8), levofloxacin (LEV, 98%; Alfa Aesar; CAS 100986–85–4), and lansoprazole (LAN, $>98\%$; Alfa Aesar; CAS 103577–45–3) were used as target pollutants. *p*-benzoquinone (*p*-BQ, $\geq 98\%$; Sigma-Aldrich; CAS 106–51–4), tert-butanol (TBA, $\geq 99\%$; Sigma-Aldrich; CAS 75–65–0), methanol (MeOH, $\geq 99.9\%$; Sigma-Aldrich; CAS 67–56–1), furfuryl alcohol (FFA, 98%; Sigma-Aldrich; CAS 98–00–0), silver nitrate (AgNO_3 , 99.8%; Panreac; 7761–88–8) and ethylenediaminetetraacetic acid (EDTA, 99.4–100.6%; Sigma-Aldrich; CAS 60–00–4) were used as scavengers. Cross-linked polystyrene (PS) microparticles were purchased from Supelco (Merck) (10 μm ; product no. 72986; Quality Level 100) as an aqueous suspension containing 10% (w/w) solids with 2% cross-linking. The reported particle size was 10 μm with standard deviation $< 0.2 \mu\text{m}$ (coefficient of variation $< 2\%$) and a density of 1.05 g cm^{-3} . Peroxymonosulfate (PMS; OXONE®; CAS 70693–62–8) was used as oxidant. Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, $\geq 99\%$; Sigma-Aldrich; CAS 7772–98–7) was used to quench residual PMS in treated samples. Milli-Q water (18 M Ω cm) was used where indicated.

2.2. Synthesis and characterization of photocatalysts

2.2.1. Synthesis of TiO_2 nanofibers via electrospinning

Two precursor solutions were prepared. Solution A was obtained by dissolving PVP (0.300 g) in EtOH (3.0 mL) under stirring for 45 min. Solution B was prepared by mixing TTIP (3.0 mL), AA (2.0 mL), and EtOH (2.0 mL) under stirring for 45 min. Solutions A and B were combined and stirred for 1 h to obtain a homogeneous spinning dope. The resulting solution was loaded into a syringe fitted with a stainless-steel needle (19 G; outer diameter ≈ 1.1 mm; length 30 mm; Sterican®, B. Braun) and processed using an electrospinning setup equipped with a rotating collector and a high-voltage power supply. Electrospinning was carried out at 20 kV with a solution flow rate of 1 mL per hour, a tip-to-collector distance of 10 cm, and a collector rotation speed of 1900 rpm, for a spinning duration of 8 h, under ambient conditions (25 °C) [50].

The as-spun fibrous product was calcined in alumina crucibles ($130 \times 30 \times 15 \text{ mm}^3$) at 420 °C in air using a heating ramp of $2 \text{ }^\circ\text{C min}^{-1}$ and a dwell time of 4 h. After calcination, an estimated mass loss of $\sim 80\%$ was observed, attributed to PVP removal and oxide crystallization. The macroscopic mat structure was not maintained after calcination and collapsed into a loose powder; accordingly, mat thickness before/after calcination was not treated as a controlled synthesis parameter. Although the macroscopic mat disintegrated, field-emission scanning electron microscopy (FE-SEM) confirmed preservation of the one-dimensional fibrous morphology at the microscopic level.

2.2.2. Synthesis of TiO_2/BiOI nanofibers by solvothermal growth

BiOI was grown on TiO_2 nanofibers by a solvothermal method. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1.22 g) and KI (0.52 g) were separately dissolved in EG (50 mL each). The KI solution was added dropwise to the $\text{Bi}(\text{NO}_3)_3$ solution under stirring. The mixture was stirred for 30 min and sonicated for 10 min to obtain a homogeneous suspension. The resulting solution was transferred into a Teflon-lined stainless-steel autoclave (100 mL). TiO_2 nanofibers were added at a loading of 1.1 mg mL^{-1} (relative to the EG solution volume) and stirred for 10 min prior to solvothermal treatment. The autoclave was heated at 160°C for 6 h and then cooled to room temperature. The collected BiOI/TiO_2 nanofibers were washed repeatedly with Milli-Q water and EtOH (96%; Panreac) to remove residual EG, filtered, and dried at 120°C for 6 h in air.

2.2.3. Materials characterization

Morphology was examined by field-emission scanning electron microscopy (FE-SEM; JEOL J-7100) coupled with energy-dispersive X-ray spectroscopy (EDX) for elemental analysis (20 kV, 10 mm WD). Semi-quantitative EDX analysis was also used to estimate the BiOI fraction in the TiO_2/BiOI samples, assuming Ti as TiO_2 and Bi/I as BiOI ; the resulting values are reported as approximate compositional estimates rather than absolute bulk loadings. Surface chemical states were analyzed by X-ray photoelectron spectroscopy (XPS; PHI Quantera SXM) using monochromated Al K α radiation with a $200 \mu\text{m}$ spot size under ultra-high vacuum. Crystal structure was determined by X-ray diffraction (XRD; PANalytical X'Pert PRO; Cu K α radiation). Photoluminescence (PL) spectra were recorded using a custom-built setup with 365 nm LED excitation (M365FP1, Thorlabs); emission was collected through a 400 nm long-pass filter (FEL400, Thorlabs) and analyzed using an Andor 193i spectrometer coupled with an Andor iDus CCD camera. Optical absorption was assessed by UV-vis diffuse reflectance spectroscopy (DRS; PerkinElmer Lambda 900). Textural properties were obtained from N_2 physisorption at 77 K (Micromeritics TriStar II). The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method, and pore-size distribution/porosity were evaluated by Barrett–Joyner–Halenda (BJH) and t-plot analyses.

2.3. Photocatalytic PMS activation experiments

2.3.1. Degradation and mineralization of SMX and multipollutant solutions

Photocatalytic tests were performed using SMX and a multipollutant (MP) solution. Prior to irradiation, catalyst powders were dispersed in the pollutant solution and kept in the dark for 30 min to establish adsorption–desorption equilibrium. For the benchmark experiments, SMX solutions were prepared at an initial concentration of 5 mg L^{-1} . MP solutions were prepared at 20 ppm total concentration, comprising SMX (5 ppm), TC (5 ppm), LEV (5 ppm), and LAN (5 ppm). The solution pH was adjusted to 7. Each experiment used 20 mL of pollutant solution containing 10 mg catalyst (0.50 g L^{-1}).

Irradiation experiments were conducted in a PennPhD Photoreactor M2 (Sigma-Aldrich) equipped with interchangeable LED modules. Visible-light tests were performed with the 450 nm module and UV-A tests with the 365 nm module. The photoreactor provides a 360° reflective irradiation environment; reaction temperature was monitored/controlled using a K-type thermocouple, and magnetic stirring was set to 400 rpm (range 100–2000 rpm). The LED output was set to 50% intensity via the photoreactor interface. Reactions were carried out in 20 mL vials placed in the photoreactor chamber and maintained at 20°C throughout irradiation.

For PMS-assisted SMX and multipollutant experiments, a freshly prepared PMS stock solution was used at 250 mM, expressed as active PMS equivalent. A volume of 200 μL of this stock solution was added to the reaction mixture to obtain a final PMS concentration of 2.5 mM in a final reaction volume of 20.0 mL. Aliquots were withdrawn at 5, 20, 40, 60, 80, and 120 min, filtered through $0.22 \mu\text{m}$ PTFE membranes, and quenched with sodium thiosulfate (0.5 M) prior to analysis. A PMS

concentration of 2.5 mM was used as a fixed benchmark oxidant concentration to compare the TiO_2/BiOI catalyst series under intensified PMS-assisted photocatalytic conditions. This concentration was not optimized for oxidant economy or process implementation.

To evaluate the effects of pollutant loading and reaction temperature under visible-light-assisted PMS activation, additional SMX experiments were performed at initial concentrations of 5, 10, and 20 mg L^{-1} and temperatures of 20, 30, and 40°C . All other operating conditions were maintained at the benchmark values: pH 7, a final reaction volume of 20 mL, a catalyst loading of 0.50 g L^{-1} , a PMS concentration of 2.5 mM, magnetic stirring at 400 rpm, and irradiation using the 450 nm LED module at 50% output. Mineralization after 120 min was determined by blank-corrected TOC analysis using the same filtration and quenching procedure applied in the benchmark experiments.

To evaluate matrix robustness, additional multipollutant experiments were performed using filtered tap water instead of Milli-Q water. The tap water was filtered through a $0.22 \mu\text{m}$ membrane before use and presented an alkalinity of $109 \text{ mg CaCO}_3 \text{ L}^{-1}$ and hardness of $113 \text{ mg CaCO}_3 \text{ L}^{-1}$, with Ca^{2+} and Mg^{2+} concentrations of 58.2 and 8.9 mg L^{-1} , respectively. The main inorganic constituents were HCO_3^- (114 mg L^{-1}), Cl^- (96.3 mg L^{-1}), and NO_3^- (4.6 mg L^{-1}), with 1.02 mg L^{-1} free Cl_2 . The four-component multipollutant solution was prepared in this filtered tap water at the same total pollutant concentration used in Milli-Q water, and TOC removal after 120 min was used as the bulk mineralization endpoint.

For SMX-only experiments, SMX concentration was quantified by UHPLC and mineralization was assessed by total organic carbon (TOC). Catalyst-free controls were performed under the same irradiation and solution conditions to evaluate direct photolysis and homogeneous PMS activation. These controls included UV-A irradiation, UV-A + PMS, visible-light irradiation, and visible light + PMS in the absence of TiO_2/BiOI catalyst. For MP experiments, treatment performance was evaluated by TOC as a bulk mineralization endpoint. Individual degradation curves for TC, LEV, LAN, and SMX in the mixture were not used to derive compound-specific kinetic parameters. The MP experiment was designed to assess net oxidative removal of the mixed organic carbon load, including parent compounds and transformation products. SMX concentrations were determined using an ultra-high-performance liquid chromatography system (UHPLC; UltiMate 3000, Thermo Fisher Scientific Inc.) equipped with a Hypersil GOLD™ C18 column ($4.6 \text{ mm} \times 250 \text{ mm}$). The mobile phase consisted of 60% (v/v) acetonitrile in water and was delivered at 1.0 mL min^{-1} with the column maintained at 30°C ; detection was performed at 270 nm. Degradation intermediates were analyzed by mass spectrometry (Micromass Quattro micro API, Waters Corp.) in positive ion mode over an m/z range of 50–1000. TOC was measured using a TOC-VCSH analyzer (Shimadzu). TOC measurements were performed with blank correction because several treated samples approached the low-carbon range after photocatalytic PMS treatment. The Shimadzu TOC-VCSH analyzer used in this work has a manufacturer-reported TC measurement range extending down to $4 \mu\text{g C L}^{-1}$ under the relevant configuration; however, the analytical figures of merit used for data interpretation were determined from blanks processed with the same filtration and quenching steps as the samples. Milli-Q water blanks, PMS-containing blanks, catalyst-contact blanks, and quenched blanks were filtered and analysed using the same protocol applied to treated samples. The method LOD and LOQ were calculated from repeated blank measurements as 3σ and 10σ , respectively, after blank correction. When residual TOC values approached the method LOQ, mineralization was interpreted conservatively as near-complete TOC removal rather than as a statistically meaningful decimal-level difference.

Reactive pathways in the TiO_2/BiOI -PMS system were examined by combining scavenger (quenching) tests with complementary, solution-phase assays that track PMS consumption and operational proxies for oxidizing flux. Experiments were conducted under the same irradiation modes used for SMX removal (UV-A, 365 nm; visible, 450 nm), in the

presence of PMS at an initial concentration of 2.5 mM. For scavenger tests, individual quenchers were added at the start of the run at a nominal concentration of 1 mM: p-benzoquinone (p-BQ, assigned to $O_2^{\bullet -}$ quenching), tert-butyl alcohol (TBA, $\bullet OH$), methanol (MeOH, $\bullet OH$ and $SO_4^{\bullet -}$), furfuryl alcohol (FFA, 1O_2), $AgNO_3$ (e- scavenging), and EDTA (h^+ scavenging). SMX degradation was then quantified after 120 min under UV-A + PMS or visible light + PMS, and compared with the corresponding “no quencher” condition. The concentration of SMX was also quantified by UHPLC. The scavenger experiments were used as qualitative pathway-sensitivity tests rather than as quantitative ROS-speciation measurements.

In parallel PMS-activation runs, residual PMS concentrations were quantified as a function of time (2 h, 8 h, 24 h) using an iodometric method followed by UV-vis analysis of the resulting I_3^- signal using UV-vis spectrophotometer (Shimadzu UV-1800). Oxidizing equivalents generated during PMS activation were further assessed with a Ce (III) oxidation assay by monitoring Ce(IV) accumulation at the same time points by UV-vis spectroscopy (same instrument) using an external Ce(IV) calibration. Hydroxyl-associated oxidative flux was evaluated using the terephthalate probe approach by quantifying hydroxyterephthalic acid (hTPA) after 2 h by fluorescence spectroscopy (AMINCO-Bowman Series 2 spectrofluorometer). Singlet oxygen was examined using Singlet Oxygen Sensor Green (SOSG, Invitrogen), with the SOSG fluorescence intensity recorded after 45 min on the same fluorometer; the signal is reported in arbitrary units and interpreted as a comparative indicator of 1O_2 -associated probe response under the tested conditions rather than as a direct, absolute quantification of 1O_2 .

2.3.1.1. Reusability and stability tests. Reusability was assessed over nine consecutive cycles using the MP solution, with TOC measured after 120 min of treatment in each cycle. After each run, the catalyst was recovered by centrifugation and rinsed four times with Milli-Q water before being transferred to a fresh MP solution for the next cycle. No pollutant-containing MP solution was used as a washing medium, and no additional chemical or thermal regeneration step was applied.

Photochemical stability was assessed by quantifying metal-ion leaching from the catalyst after visible-light irradiation for 2 h in the presence of PMS. Catalyst integrity was evaluated by measuring bismuth and titanium concentrations in the reaction medium using inductively coupled plasma optical emission spectroscopy (ICP-OES; Optima 8300, PerkinElmer) for ppm-level concentrations and inductively coupled plasma mass spectrometry (ICP-MS; NexION 2000, PerkinElmer) for ppb-level detection. Prior to analysis, liquid samples were filtered through 0.22 μm PTFE membranes. The release of iodine species was examined by anion-exchange chromatography with postcolumn reaction and UV/visible detection. Measurements were performed using a Dionex DX-500 ion chromatography system equipped with a Dionex PC 10 reagent delivery module, an ASRS-I membrane-exchange suppressor, and a Spectroflow 773 absorbance detector. Iodide was separated on a Dionex AG11/AS11 column using an eluent of 60 mM sodium bromide and 1 mM sodium hydroxide. Postcolumn reaction with 5 μM bromine in 2 mM NaOH converted iodide to IBr_2 , which was detected at 249.5 nm. All reagents were of the highest purity, and standard solutions were freshly prepared in Milli-Q water.

2.3.1.2. Biototoxicity assessment of treated water. Biototoxicity of treated MP water was evaluated using a seed germination and early growth inhibition assay with lettuce (*Lactuca sativa*). Residual PMS in PMS-treated samples was neutralized using $Na_2S_2O_3$. Controls included Milli-Q water, a PMS-water solution, and an untreated MP solution. Twelve lettuce seeds were placed in each 90 mm polystyrene Petri dish lined with five layers of filter paper. Each dish was irrigated with 5.0 mL of the corresponding sample and incubated for 5 days in closed chambers under dark, humid conditions at 20 °C. Germination was defined as a radicle length ≥ 2 mm, and radicle lengths were measured after

incubation. All assays were performed in triplicate.

Relative germination (RG), relative root elongation (RRE), and germination index (GI) were calculated as:

$$RG(\%) = \frac{G_s}{G_c} \cdot 100$$

$$RRE(\%) = \frac{L_s}{L_c} \cdot 100$$

$$GI(\%) = \frac{RG(\%) \cdot RRE(\%)}{100}$$

Where G_s and G_c denote the number of germinated seeds in the sample and control (Milli-Q water), respectively, and L_s and L_c denote the corresponding mean root lengths (mm) of the germinated seeds. As phytotoxicity screening, $GI > 80\%$ indicates low or negligible phytotoxicity, $GI = 50\text{--}80\%$ indicates moderate phytotoxicity, and $GI < 50\%$ indicates high phytotoxicity.

2.3.2. Degradation of microplastics

Microplastics degradation experiments were performed using cross-linked PS microparticles as a model particulate pollutant. The PS suspension was prepared at 20 ppm (solids) in Milli-Q water. Reactions were carried out at a total working volume of 1.0 mL in glass vials containing 1 mg of catalyst. The suspension was mixed for 30 min prior to PMS addition. For the microplastic experiments, PMS was added from the same freshly prepared 250 mM PMS stock solution. A volume of 10 μL was used to obtain a final PMS concentration of 2.5 mM in the 1.0 mL reaction volume. Irradiation was conducted in a SynLED Parallel Photoreactor (Sigma-Aldrich) equipped with bottom-lit LEDs (465–470 nm) arranged in a 4×4 reaction-block array, providing a consistent illumination geometry (LED angle 45°) and a nominal luminous flux of 130–140 lm. The photoreactor incorporates an integrated cooling fan to maintain a constant reaction temperature (20 °C) across parallel runs. Reactions were magnetically stirred throughout irradiation using an IKA round-plate stirrer. Experiments were performed for irradiation times of 2, 4, 6, and 24 h. After irradiation, 100 μL of each suspension were deposited onto fluorine-doped tin oxide glass pieces and dried in air. Prior to FE-SEM observation, the FTO substrates containing microplastics and catalyst were carbon-coated to ensure sufficient electrical conductivity for imaging. Degradation and morphological changes of PS microparticles were assessed qualitatively by FE-SEM by comparing particle surface features and structural integrity before and after treatment.

The 1.0 mL microplastic experiments were used to evaluate morphological changes of PS microparticles by FE-SEM and were not used for direct gravimetric determination of total polymer mass loss. Because the initial PS mass in these tests was in the microgram range and substantially lower than the catalyst mass, quantitative TOC and gravimetric analyses were performed separately in scaled-up experiments. For this purpose, 24 h microplastic degradation experiments were repeated using 250 mL suspensions under the same PS concentration and irradiation/PMS conditions. After treatment, the suspension was passed through a 10.0 μm nylon filter to retain the catalyst fibers and residual micrometer-sized polymer particles. The filtrate was collected as the aqueous/sub-10 μm fraction and analyzed by TOC using a Shimadzu TOC-VCSH analyzer. This fraction was considered to contain dissolved organic carbon, low-molecular-weight oxidation products, and sub-10 μm polymer-derived fragments able to pass through the filter. In parallel, aliquots of the filtrate were evaporated to dryness, and the remaining non-volatile residue was weighed using an analytical balance with a precision of 0.01 mg. Values were corrected using the corresponding catalyst/PMS blanks without PS and are reported as operational indicators of polymer fragmentation and solubilization rather than as direct total microplastic mass-loss values. Experiments were performed in three independent replicates. Catalyst-

only control experiments were also performed to assess possible catalyst carry-over through the 10.0 μm filter. Catalyst suspensions without PS were processed under the same filtration protocol. The resulting filtrates were dried on conductive substrates and examined by FE-SEM. No appreciable TiO_2/BiOI fibers or catalyst fragments were observed in the dried filtrates, indicating that catalyst passage through the filter was negligible within the resolution and sampling limits of FE-SEM analysis.

3. Results and discussion

3.1. Material synthesis and characterization

TiO_2 is widely used in photocatalysis, yet its large band gap restricts photoexcitation largely to the UV range [51–53]. To extend light harvesting toward the visible, electrospun TiO_2 nanofibers were used as a 1D scaffold for the growth of BiOI, a narrower-band-gap semiconductor, yielding a coated-fiber heterostructure (Fig. 1a) [49,54]. The architecture was tuned by solvothermal growth at 160 $^\circ\text{C}$ while varying the treatment time (2–16 h), using reaction time as a controlled synthesis parameter to regulate BiOI nucleation, surface coverage, and overgrowth on the TiO_2 fibrous scaffold [29,55].

FE-SEM micrographs of the pristine TiO_2 sample (Fig. 1b) show an

interwoven network of continuous fibers with apparent diameters in the 500–2500 nm range. The mat exhibits frequent fiber–fiber junctions and open inter-fiber voids typical of electrospun architectures. At the resolution of the images shown, the TiO_2 fiber surfaces appear comparatively smooth, without obvious particulate decoration.

BiOI was grown onto TiO_2 via solvothermal treatment for 2 h (TBO1), 4 h (TBO2), 6 h (TBO3), and 16 h (TBO4). Across the series, FE-SEM indicates a clear time-dependent evolution from sparse surface features to a more continuous sheath surrounding the fibers (Fig. 1d–g). After 2 h (TBO1, Fig. 1d), discrete plate-like crystallites appear on the TiO_2 surface. This platelet morphology is consistent with BiOI morphologies commonly reported in the literature [49], although FE-SEM alone cannot verify phase identity or composition. Increasing the treatment time to 4 h (TBO2, Fig. 1e) increases the surface coverage and roughness, producing a densely textured, platelet-decorated BiOI-rich outer layer. After 6 h (TBO3, Fig. 1f), the fibers appear encapsulated by a nearly continuous, thicker shell with a granular/rough texture, consistent with extensive overgrowth relative to the earlier stages. Extending the solvothermal time to 16 h (TBO4, Fig. 1g) preserves a coated-fiber morphology while suggesting further thickening and/or coarsening of the outer layer in the regions imaged.

The time-programmed evolution from sparse platelets to “hairy” and

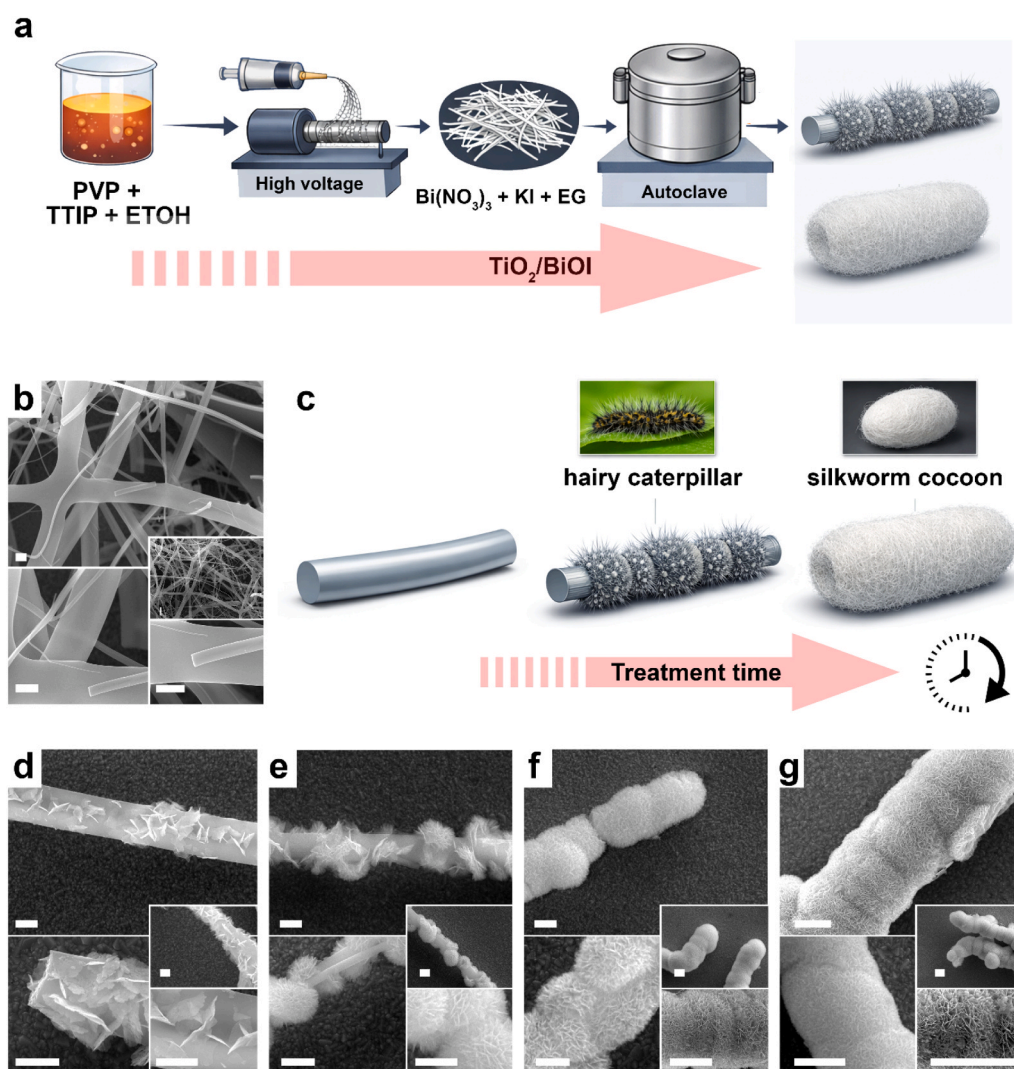


Fig. 1. (a) Schematic illustration of the synthesis route for electrospun TiO_2 nanofibers and subsequent solvothermal BiOI growth. (b) FE-SEM micrograph of pristine TiO_2 nanofibers. (c) Schematic depiction of the progressive evolution from sparsely decorated fibers to rough platelet-decorated and shell-like coated-fiber morphologies with increasing solvothermal time; the terms ‘hairy’ and ‘cocoon-like’ are used only as descriptive visual analogies. FE-SEM micrographs of TiO_2/BiOI fibers after solvothermal treatment at 160 $^\circ\text{C}$ for (d) 2 h (TBO1), (e) 4 h (TBO2), (f) 6 h (TBO3), and (g) 16 h (TBO4). Scale bar: 1000 nm.

“cocoon-like” coated fibers (Fig. 1c) is relevant from a biomimetic-architecture standpoint because it generates a hierarchical, optically complex medium rather than a simple planar coating [35,56,57]. The electrospun mat provides a three-dimensional framework with inter-fiber voids and numerous junctions, which creates multiple liquid/solid interfaces and a broad distribution of incidence angles for incoming light [58,59]. On this scaffold, the progressive BiOI growth adds secondary and tertiary features: early-stage platelet-like crystallites introduce faceted, anisotropic scatterers on the fiber surface, whereas longer treatments yield a more continuous, roughened outer sheath that increases surface corrugation and geometric tortuosity at the sub-micrometric scale. Together, these length-scale levels (mat-level void space, fiber-level curvature, and nanoscale-to-submicron surface texturing) are consistent with architectures used in nature to manage photon flux [60] (e.g., anti-reflection textures and diffuse scattering surfaces), where the objective is to suppress specular reflection and

redistribute light into the interior of the medium. From an optical perspective, a random fibrous network can act as a “photon management” layer by increasing the probability of multiple scattering events, effectively lengthening the optical path within a given catalyst thickness [61]. This is particularly relevant for semiconductors that benefit from enhanced photon residence time in the absorbing phase: instead of a single pass through a flat film, photons can undergo repeated redirection between neighboring fibers and across junction-rich regions, increasing the chance of absorption by the BiOI coating (and, where exposed, by TiO_2) [62,63]. The coated-fiber geometry also tends to reduce angular sensitivity: because fibers are oriented stochastically and present curved surfaces to the incident beam, photon capture can remain efficient under non-normal illumination, which is a practical advantage under real irradiation conditions where collimation is imperfect [64,65]. At the same time, the BiOI overgrowth introduces light–matter interaction sites across the full mat depth, which can mitigate the “surface-only”

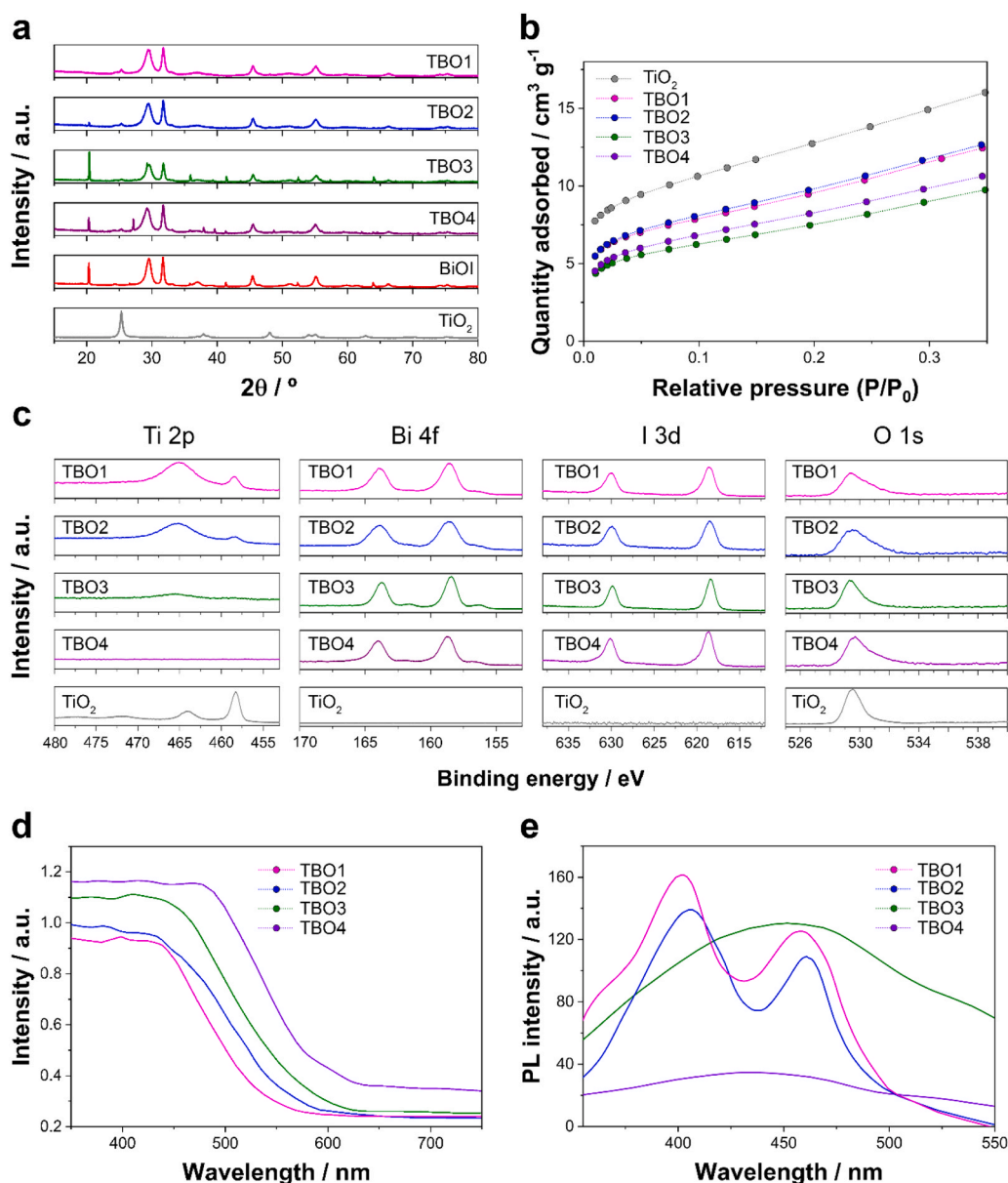


Fig. 2. (a) X-ray diffraction (XRD) patterns showing anatase TiO_2 reflections together with additional peaks consistent with tetragonal BiOI for the coated samples. (b) N_2 physisorption data used to derive BET surface area of pristine TiO_2 and TiO_2/BiOI nanofibers. (c) X-ray photoelectron spectroscopy (XPS) core-level spectra (binding energies referenced to C 1 s at 284.8 eV) highlighting Ti 2p, Bi 4 f, I 3d, and O 1 s regions for the pristine TiO_2 and composite fibers. (d) UV–vis diffuse reflectance spectra (DRS) of the TiO_2/BiOI series illustrating the progressive extension of absorption into the visible region with increasing BiOI growth time. (e) Photoluminescence (PL) emission spectra of the TiO_2/BiOI samples showing solvothermal-time-dependent changes in emission intensity and band shape.

excitation typical of dense, smooth films.

XRD patterns were collected to identify the crystalline phases present in the pristine TiO_2 nanofibers and after solvothermal BiOI growth (Fig. 2a). The TiO_2 sample exhibits the characteristic reflections of anatase, including the dominant (101) peak at $2\theta \approx 25.3^\circ$. After solvothermal treatment in the presence of Bi and I precursors, additional reflections appear in all TiO_2/BiOI samples at $2\theta \approx 20.3^\circ$, 29.4° , 31.7° , 37.1° , 45.4° , and 55.1° , which are consistent with tetragonal BiOI (JCPDS 73–2062) [29] and match the reference BiOI pattern shown in Fig. 2a. In the TiO_2/BiOI samples, the anatase (101) reflection at $2\theta \approx 25.3^\circ$ is strongly attenuated and is not distinctly resolved in the plotted patterns. This attenuation is attributed to the dominant diffraction contribution of the Bi/I-containing BiOI phase, partial masking of the TiO_2 scaffold by the BiOI overlayer, possible broadening of the electrospun anatase contribution, and intensity normalization to the stronger BiOI reflections. Therefore, XRD confirms the formation of crystalline BiOI on the TiO_2 -derived fibrous scaffold, whereas retention of the TiO_2 component in the composites is supported by the synthesis route, FE-SEM morphology, EDX compositional analysis, and the Ti 2p XPS signal [49]. Changes in relative peak intensities across TBO1–TBO4 should be interpreted cautiously because they can reflect both preferred orientation effects associated with platelet-like BiOI crystallites and the progressive increase in BiOI content with solvothermal growth time. To provide compositional support for this trend, semi-quantitative EDX-derived BiOI loading estimates were added for the TBO series. The estimated BiOI fraction increased monotonically from approximately 7% for TBO1–23% for TBO2, 39% for TBO3, and 67% for TBO4. These values support the compositional trend inferred from FE-SEM, XRD, and XPS, namely the progressive enrichment of the TiO_2 fibers with BiOI during solvothermal treatment. Because EDX provides semi-quantitative information and probes a finite interaction volume, these values should be regarded as approximate loading estimates rather than exact bulk mass fractions. Nevertheless, the monotonic increase is consistent with the observed morphological transition from discrete BiOI platelets to more continuous hairy/cocoon-like coatings.

Nitrogen adsorption measurements were used to evaluate the adsorption-accessible textural properties (Fig. 2b). The BET surface area decreases from $47.1 \text{ m}^2 \text{ g}^{-1}$ for pristine TiO_2 to $36.1\text{--}37.5 \text{ m}^2 \text{ g}^{-1}$ for TBO1–TBO2 and $28.6\text{--}31.4 \text{ m}^2 \text{ g}^{-1}$ for TBO3–TBO4. A similar trend is observed for the single-point total pore volume reported for pores $< 3.0 \text{ nm}$, which decreases from $0.0248 \text{ cm}^3 \text{ g}^{-1}$ (TiO_2) to $0.0193\text{--}0.0196 \text{ cm}^3 \text{ g}^{-1}$ (TBO1–TBO2) and $0.0151\text{--}0.0164 \text{ cm}^3 \text{ g}^{-1}$ (TBO3–TBO4). By contrast, the adsorption average pore width estimated as $4 V/A$ remains essentially constant at $\sim 2.09\text{--}2.14 \text{ nm}$ across all samples. Taken together, these data are consistent with progressive surface coverage by BiOI reducing the adsorption-accessible surface area and small-pore volume while leaving the characteristic scale of the remaining adsorption-accessible porosity largely unchanged.

The term ‘hierarchical’ is used here as a morphological descriptor of the multi-length-scale fibrous architecture observed by FE-SEM, including inter-fiber voids, fiber curvature, platelet-like BiOI features, and rough shell-like coatings. No quantitative fractal dimension is assigned, because SEM- and adsorption-derived fractal dimensions are strongly dependent on image processing, pressure range selection, and model assumptions and are not required for the present structure-activity discussion.

XPS was employed to probe the surface composition of the coated fibers (Fig. 2c), with the C 1s signal at 284.8 eV used as the binding-energy reference. The Ti 2p signal is clearly observed for pristine TiO_2 [52,66] and remains detectable for the coated samples, but it is progressively attenuated with increasing solvothermal time, in line with the formation of a thicker BiOI overlayer that increasingly masks the underlying TiO_2 within the XPS sampling depth. The TiO_2/BiOI samples show Bi 4f doublet peaks at $\sim 159.2 \text{ eV}$ (Bi 4f_{7/2}) and $\sim 164.5 \text{ eV}$ (Bi 4f_{5/2}), consistent with Bi³⁺ in bismuth oxyhalide environments, and I 3d peaks at $\sim 619.5 \text{ eV}$ (I 3d_{5/2}) and $\sim 630.9 \text{ eV}$ (I 3d_{3/2}), consistent with

iodide in BiOI [55,67]. The O 1s region presents a broadened feature centered around $\sim 530 \text{ eV}$ with a higher-binding-energy shoulder near $\sim 531.3 \text{ eV}$, which is commonly associated with surface hydroxyls and/or adsorbed water. Accordingly, the O 1s signal is best interpreted here as evidence for mixed oxide/oxyhalide oxygen environments plus surface hydroxylation rather than as a unique marker of a specific interfacial bond.

The optical response of the coated fiber series was assessed by UV–vis DRS (Fig. 2d). As the solvothermal growth time increases from TBO1 to TBO4, the spectra show progressively stronger absorption in the visible region and an overall redshift of the absorption edge, consistent with the increasing contribution of BiOI to the TiO_2 -based fibrous scaffold. [68]. The corresponding Tauc plots, including the tangent extrapolation lines used for estimating the apparent optical band gaps, are provided in Figure S1. The apparent band gaps are estimated as 2.41 eV for TBO1, 2.28 eV for TBO2, 2.31 eV for TBO3, and 2.16 eV for TBO4. These values support an overall narrowing of the apparent optical gap with increasing BiOI growth, although the very similar values obtained for TBO2 and TBO3 should not be interpreted as a strictly monotonic change. Because hierarchical electrospun mats can exhibit different scattering backgrounds as BiOI loading, coating roughness, and shell thickness evolve, the Tauc-derived values are used here as comparative optical descriptors within the series rather than as absolute electronic band gaps or direct evidence of specific band-edge positions [69].

PL emission spectra of the TiO_2/BiOI series (Fig. 2e) change systematically with solvothermal growth time. TBO1 shows the highest emission intensity, and the PL signal is progressively quenched for TBO2–TBO4. The emission envelope also broadens and becomes less structured, most evident for TBO3, indicating that the dominant emissive pathways are modified as the BiOI overlayer develops. In semiconductor composites, such quenching is commonly consistent with reduced radiative recombination and/or the introduction of additional non-radiative decay pathways, potentially including interfacial carrier transfer and defect-mediated trapping [70,71]. However, because these samples are optically heterogeneous fiber mats, PL intensity can also be affected by differences in excitation attenuation, scattering/out-coupling, and re-absorption as BiOI loading increases, as well as by sample packing and measurement geometry. The PL trends therefore support a change in recombination/emission dynamics across the series with increasing BiOI coverage, while their functional impact should be assessed alongside the DRS absorption trends and the photocatalytic performance.

3.2. Photocatalytic PMS activation experiments

3.2.1. Degradation and mineralization of SMX and multipollutant solutions

SMX removal was evaluated under UV-A (365 nm) or visible light (450 nm) using the TiO_2/BiOI series (TBO1–TBO4), with and without PMS (2.5 mM), at pH 7 and 20°C (SMX 5 ppm; catalyst loading 0.50 g L^{-1}). Prior to irradiation, suspensions were equilibrated in the dark for 30 min. Dark adsorption increased modestly with solvothermal growth time, from $\sim 8\%$ for TBO1 to $\sim 15\%$ for TBO4. This trend should not be interpreted as an increase in BET-accessible surface area, since N_2 physisorption shows that the specific surface area decreases as BiOI coverage grows. Instead, the higher dark uptake is attributed to changes in aqueous interfacial affinity introduced by the BiOI-rich overlayer and the associated modification of surface chemistry. N_2 -BET probes dry gas-accessible surface area and small-pore volume, whereas SMX adsorption from water also depends on surface polarity, hydroxylation, local surface composition, and specific interactions with the outer BiOI-containing surface. Accordingly, the adsorption trend is discussed here as a modest change in SMX–surface affinity rather than as evidence of increased textural surface area. Control experiments were added to distinguish direct photolysis, homogeneous light-assisted PMS activation, and heterogeneous TiO_2/BiOI -mediated PMS activation. In the absence of catalyst, UV-A irradiation alone produced $5.7 \pm 0.3\%$ SMX

degradation after 80 min, while UV-A + PMS increased SMX degradation to $9.2 \pm 0.5\%$ over the same period (Table S1). The corresponding TOC removals after 120 min were only $2.9 \pm 1.4\%$ and $4.9 \pm 1.2\%$, respectively (Table S2). Visible-light controls showed even lower background activity, with $2.8 \pm 0.2\%$ SMX degradation under visible light alone and $7.4 \pm 0.4\%$ under visible light + PMS after 80 min. These results confirm that light-assisted PMS activation can occur in the absence of catalyst, particularly under UV-A irradiation, but its contribution is minor under the present conditions.

Under UV-A irradiation without PMS (Figs. 3a and 3e), all TiO_2/BiOI samples promote substantial SMX degradation, with a clear dependence on BiOI growth time. After 80 min, degradation increases from 59.5% (TBO1) to 80.8% (TBO4), and TOC removal after 120 min increases from 62.5% (TBO1) to 79.2% (TBO4). Apparent pseudo-first-order fits ($\ln(C/C_0)$ vs time, 0–60 min) give increasing rate constants from $1.1 \times 10^{-2} \text{ min}^{-1}$ (TBO1) to $2.0 \times 10^{-2} \text{ min}^{-1}$ (TBO4), consistent with accelerated transformation as the BiOI fraction and surface development increase. The persistent gap between SMX conversion ($\geq 59\text{--}81\%$ at 80 min) and TOC removal (62–79% at 120 min) indicates that a portion of SMX is converted into organic intermediates that require longer irradiation or stronger oxidizing conditions for deep oxidation.

Adding PMS under UV-A (UV-A+PMS) produces a pronounced acceleration and drives mineralization close to completion for all TiO_2/BiOI samples (Figs. 3b and 3f). SMX degradation reaches 90–96% already at 60 min and 92.9–98.1% at 80 min, while TOC removal after 120 min is 96.5–98.8%. The corresponding apparent k_{obs} values (0–60 min) rise to $3.9\text{--}5.3 \times 10^{-2} \text{ min}^{-1}$, with TBO3 showing the highest k_{obs} ($5.3 \times 10^{-2} \text{ min}^{-1}$). These trends are consistent with PMS providing an additional oxidative channel under irradiation, enabling faster SMX breakdown and substantially enhancing deep oxidation relative to UV-A photocatalysis alone. Differences among TBO1–TBO4 become comparatively small in terms of final mineralization (all $\geq 96\%$), suggesting that, under UV-A + PMS, the system is less sensitive to the precise degree of BiOI overgrowth once effective PMS activation is established.

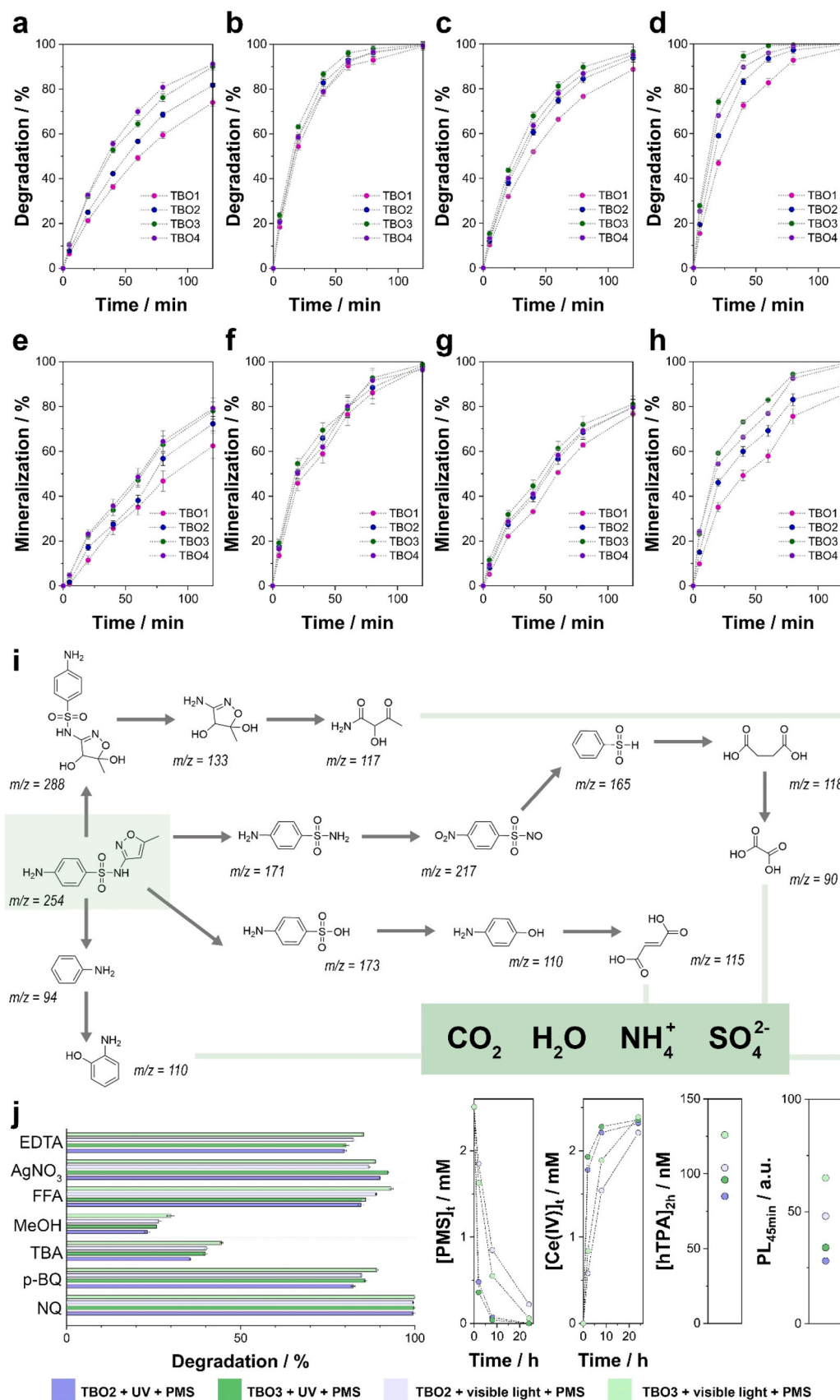
Under visible-light irradiation without PMS (Figs. 3c and 3g), the TiO_2/BiOI series remains active for SMX degradation, consistent with the visible absorption introduced by BiOI and the light-management features of the fibrous architecture discussed above. After 80 min, degradation increases from 76.6% (TBO1) to 89.6% (TBO3) and then slightly decreases to 86.7% (TBO4). Apparent k_{obs} values mirror this trend, increasing from $1.8 \times 10^{-2} \text{ min}^{-1}$ (TBO1) to $2.8 \times 10^{-2} \text{ min}^{-1}$ (TBO3), followed by a modest decrease for TBO4 ($2.5 \times 10^{-2} \text{ min}^{-1}$). Despite the high SMX conversion, mineralization under visible alone remains moderate, reaching 76.7–81.1% TOC removal at 120 min, which again points to accumulation of partially oxidized intermediates when PMS is absent. The PMS-free systems should be mechanistically distinguished from PMS-assisted operation. In the absence of PMS, sulfate-radical-type oxidants generated from PMS are not available, and SMX transformation must arise from intrinsic TiO_2/BiOI photocatalysis. Under UV-A irradiation, both TiO_2 and BiOI may contribute to photo-induced charge generation, whereas under visible irradiation the response is mainly associated with BiOI absorption and interfacial charge separation in the TiO_2/BiOI heterostructure. The likely oxidative channels include direct oxidation by photogenerated holes, formation of $\bullet\text{OH}$ through oxidation of surface hydroxyl groups or water, and reduction of dissolved O_2 by photogenerated electrons to yield $\text{O}_2^{\bullet-}$ and related oxygen-derived intermediates. These pathways are consistent with the substantial PMS-free SMX conversion observed under both UV-A and visible light. However, because dedicated PMS-free scavenger or EPR experiments were not performed, the relative contribution of each reactive species cannot be quantified. Accordingly, PMS-free activity is discussed as intrinsic photocatalytic oxidation, whereas the detailed scavenger/probe-based ROS assignment is restricted to PMS-assisted systems.

Visible-light irradiation combined with PMS (visible light + PMS)

yields the most differentiated performance across the series and provides the clearest indication of an optimal BiOI growth extent (Figs. 3d and 3h). SMX degradation accelerates markedly relative to visible alone, reaching 82.6–99.2% at 60 min and 92.7–99.5% at 80 min. TOC removal after 120 min also increased substantially, from $85.4 \pm 3.5\%$ for TBO1 and $89.5 \pm 2.6\%$ for TBO2 to near-complete mineralization for TBO3 and TBO4. Because the SMX-only experiments start from a low initial carbon concentration, TOC values close to complete mineralization approach the low-carbon range of the analytical method. The near-complete TOC removals reported for the best-performing conditions were therefore blank-corrected using Milli-Q water, PMS-containing, catalyst-contact, and quenched blanks processed under the same conditions as the samples. When residual TOC approached the method LOQ, the results were interpreted as near-complete mineralization rather than as evidence of statistically meaningful differences at the decimal level. The apparent k_{obs} values, recalculated from the initial linear region of the $\ln(C/C_0)$ plots, span $3.2 \times 10^{-2} \text{ min}^{-1}$ for TBO1– $7.3 \times 10^{-2} \text{ min}^{-1}$ for TBO3 under visible light + PMS (Table S3). For TBO3, the fitting interval was restricted to 0–40 min because SMX degradation reached 99.2% at 60 min, placing the reaction close to the plateau region. The recalculated half-life is $t_{1/2} \approx 9.5 \text{ min}$, and TBO3 remains the fastest catalyst in the series. The slight drop in conversion rate from TBO3 to TBO4 under visible and visible light + PMS, together with the reduced BET surface area and the cocoon-like overgrowth seen by FE-SEM for the longest solvothermal time, is consistent with a trade-off at high BiOI coverage: further thickening may increase optical density while partially masking adsorption-accessible surface and/or constraining transport through the coated network. This balance is less apparent under UV-A + PMS, where the oxidation capacity is sufficiently high that near-complete mineralization is achieved across the series.

The comparison between PMS-free and PMS-assisted experiments clarifies the specific role of PMS in the TiO_2/BiOI system. The catalysts are intrinsically photocatalytically active, as shown by the substantial SMX degradation and TOC removal obtained without PMS under both UV-A and visible irradiation. Therefore, PMS is not required to initiate SMX transformation. Its main contribution is to accelerate oxidation and, more importantly, to increase the extent of mineralization. Under UV-A irradiation, TOC removal after 120 min increased from 62.5 to 79.2% without PMS to 96.5–98.8% with PMS. Under visible light, the effect was most evident for TBO3, for which TOC removal increased from $81.1 \pm 3.7\%$ without PMS to near-complete mineralization after blank correction with PMS. The early-time data show the same trend: for TBO3 under visible light, SMX degradation at 60 min increased from $81.2 \pm 1.9\%$ to $99.2 \pm 1.0\%$ after PMS addition, while TOC removal increased from $61.3 \pm 3.2\%$ to $82.9 \pm 0.5\%$. These results indicate that PMS mainly enhances the oxidative depth of the process by promoting further oxidation of SMX-derived intermediates, rather than simply increasing apparent parent-compound removal. The PMS concentration used in this work should also be interpreted carefully. A concentration of 2.5 mM was selected as a fixed benchmark condition to compare the TiO_2/BiOI series under intensified PMS-assisted photocatalytic operation. It was not optimized for oxidant economy or process implementation.

The selection of TBO3 as the best-performing sample arises from the balance between BiOI growth, interfacial heterostructure formation, optical response, and surface accessibility across the TBO series. At short solvothermal times, TBO1 and TBO2 contain lower BiOI fractions and less developed surface coverage, limiting visible-light harvesting and the number of TiO_2/BiOI interfacial sites available for charge separation and PMS activation. Increasing the growth time to 6 h produces TBO3, where the fibers are covered by a more continuous hierarchical BiOI-rich coating while still retaining an open, roughened fibrous morphology. This architecture provides stronger visible absorption, modified recombination/emission behavior, and sufficient accessible surface for SMX adsorption and interfacial PMS activation. Further extension to 16 h gives TBO4, which contains the highest BiOI fraction but also



(caption on next page)

Fig. 3. Photocatalytic degradation/mineralization of SMX and mechanistic assessment of PMS activation over TiO_2/BiOI nanofibers (TBO1–TBO4). (a–d) SMX degradation (5 ppm) as a function of time using TBO1–TBO4 under (a) UV-A irradiation, (b) UV-A + PMS, (c) visible irradiation, and (d) visible + PMS. (e–h) SMX mineralization (TOC removal) under the corresponding conditions: (e) UV-A, (f) UV-A + PMS, (g) visible, and (h) visible + PMS. PMS was added at 2.5 mM (nominal) in the PMS-assisted tests. (i) Proposed SMX transformation pathway over TBO3 under visible light + PMS, based on detected intermediates (m/z) and leading to ultimate mineralization products (CO_2 , H_2O , NH_4^+ , and SO_4^{2-}). (j) Scavenger quenching experiments (1 mM) under UV-A + PMS and visible + PMS using TBO2 and TBO3, reported as SMX degradation after 120 min; NQ denotes the no-quencher control. Quenchers and primary targets: *p*-benzoquinone (*p*-BQ, $\text{O}_2^{\cdot-}$), tert-butanol (TBA, $\cdot\text{OH}$), methanol (MeOH, $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$), furfuryl alcohol (FFA, $^1\text{O}_2$), AgNO_3 (e^- scavenger), and EDTA (h^+ scavenger). Right panels in (j): PMS consumption and probe assays during photocatalytic PMS activation over TBO2 and TBO3 under UV-A and visible irradiation: residual PMS at 2, 8, and 24 h (iodometric method, UV–vis detection of I_3^-), Ce(IV) accumulation at the same time points from a Ce(III) oxidation assay (UV–vis; external Ce(IV) calibration) as an indicator of oxidizing equivalents, hTPA formed after 2 h (terephthalate fluorescence probe) as an $\cdot\text{OH}$ -associated response, and SOSG fluorescence after 45 min (a. u.) as a comparative indicator of $^1\text{O}_2$ -associated probe response (not an absolute $^1\text{O}_2$ quantification). Initial PMS concentration in the mechanistic runs was 2.51 mM. Error bars represent mean $\pm$ standard deviation ($n = 3$).

shows cocoon-like overgrowth and lower BET-accessible surface area. This excessive coverage can increase optical density while partially masking adsorption-accessible regions and/or constraining transport through the coated network. The catalytic trends are consistent with this trade-off: under visible light + PMS, TBO3 gives the fastest SMX degradation kinetics and the highest TOC removal, whereas TBO4 does not provide further improvement despite its higher BiOI loading. Thus, TBO3 is identified as the best-performing catalyst within the tested series because it provides the most favorable compromise between visible-light absorption, TiO_2/BiOI interfacial contact, surface accessibility, and PMS-assisted oxidative throughput. For the primary comparison of the TBO1–TBO4 series, catalyst loading, PMS dose, pH, initial pollutant concentration, irradiation intensity, temperature, and water-matrix composition were fixed to isolate the effect of BiOI growth time. A separate concentration–temperature matrix was subsequently used to evaluate process robustness beyond the benchmark condition. Although these additional experiments establish systematic endpoint trends, complete multivariable optimization and determination of interaction effects, kinetic parameters, and apparent activation energies would require a dedicated factorial design supported by time-resolved measurements.

The robustness of the visible-light + PMS process toward changes in pollutant loading and reaction temperature was further evaluated using initial SMX concentrations of 5, 10, and 20 mg L^{-1} at 20, 30, and 40 $^\circ\text{C}$, while maintaining the catalyst loading and PMS concentration at 0.50 g L^{-1} and 2.5 mM, respectively (Table S4). At constant temperature, increasing the initial SMX concentration generally decreased the 120-min mineralization endpoint. At 20 $^\circ\text{C}$, TOC removal decreased from $85.4 \pm 3.5\%$ to $76.7 \pm 0.9\%$ for TBO1 and from $89.5 \pm 2.6\%$ to $81.9 \pm 1.2\%$ for TBO2 when the SMX concentration was increased from 5 to 20 mg L^{-1} . TBO3 and TBO4 were less affected, retaining mineralization values of $97.2 \pm 1.4\%$ and $95.2 \pm 0.4\%$, respectively, at 20 mg L^{-1} . The lower endpoint at increased pollutant loading is consistent with the larger organic-carbon burden and greater competition between SMX and its transformation products for the oxidative flux generated at fixed catalyst and PMS concentrations. Increasing the reaction temperature improved mineralization across the catalyst series. At 20 mg L^{-1} SMX, raising the temperature from 20 to 40 $^\circ\text{C}$ increased TOC removal from $76.7 \pm 0.9\%$ to $88.9 \pm 1.4\%$ for TBO1 and from $81.9 \pm 1.2\%$ to $92.4 \pm 0.8\%$ for TBO2. Under the same conditions, TBO3 increased from $97.2 \pm 1.4\%$ to $\geq 99.0\%$, while TBO4 increased from $95.2 \pm 0.4\%$ to $\geq 99.0\%$. At 40 $^\circ\text{C}$, TBO3 and TBO4 achieved near-complete mineralization throughout the investigated concentration range. These results indicate that the intermediate-to-high BiOI growth states provide greater resilience toward increased pollutant loading and that higher temperature accelerates the overall PMS-assisted oxidative process.

Overall, the SMX experiments separate two effects. First, BiOI growth enables strong visible-light-driven SMX conversion in the coated-fiber architecture, with the apparent rate reaching a maximum at intermediate solvothermal time. Second, PMS addition mainly increases the oxidative depth of the process rather than simply initiating SMX degradation. This is most evident from the TOC data: under visible

irradiation, mineralization increases from 76.7 to 81.1% without PMS to $85.4\text{--}\geq 99.0\%$ with PMS, depending on the catalyst. Therefore, PMS-assisted operation should be interpreted as an intensified oxidation regime that promotes further transformation of SMX-derived intermediates, while the TBO3 morphology provides the most effective balance between light harvesting, interfacial charge separation, and accessible reactive sites under the benchmark conditions used here.

For TBO3 under visible light + PMS, LC–MS analysis was used to construct a tentative transformation map for SMX (Fig. 3i and Table S5). The parent compound is assigned to protonated SMX at $m/z = 254$. The signal at $m/z = 288$ is heavier than the parent ion and is therefore not interpreted as a cleavage fragment. Instead, it is tentatively attributed to a higher-mass oxygenated SMX-derived intermediate formed after initial oxidative functionalization of SMX under PMS-assisted photocatalytic conditions. Further transformation appears to proceed through cleavage and oxidation around the sulfonamide group. The ions at $m/z = 171$, 173, 217, and 165 may be assigned to sulfanilamide-type and oxidized sulfonyl/aromatic fragments, consistent with S–N/S–C bond cleavage and subsequent oxidation of the sulfonamide-containing moiety [72, 73]. In parallel, the ions at $m/z = 133$ and 117 are consistent with oxygenated fragments derived from the isoxazole-containing part of SMX, while $m/z = 94$ is tentatively assigned to an aniline-type fragment generated after cleavage of the SMX framework [74]. Further hydroxylation, ring opening, and oxidative fragmentation are supported by lower-mass signals such as $m/z = 110$, 115, 118, and 90, which are consistent with smaller oxygenated products formed during advanced oxidation. These assignments should be treated with caution because nominal LC–MS signals do not uniquely define molecular structures, and some m/z values may correspond to isobaric products or structurally related fragments. Nevertheless, the detected product distribution is chemically consistent with a sequence involving initial oxidative functionalization of SMX, cleavage of the sulfonamide framework, fragmentation of aromatic and isoxazole-derived moieties, and progressive oxidation toward low-molecular-weight products, in agreement with the high TOC removal observed under visible light + PMS [75].

The scavenger results should be interpreted qualitatively. Endpoint inhibition experiments provide information on pathway sensitivity, but they do not quantify the concentration or fractional contribution of individual ROS. Therefore, scavenger tests under UV-A + PMS and visible light + PMS provide consistent qualitative evidence that radical pathways dominate SMX oxidation for both TBO2 and TBO3, while also indicating that multiple reactive channels operate in parallel (Fig. 3j). In the absence of quenchers, SMX removal at 120 min is essentially complete for all conditions considered (99.5–100%). Adding TBA reduces degradation to 35.4–39.8% under UV-A + PMS and 40.1–44.5% under visible light + PMS, indicating that $\cdot\text{OH}$ -accessible oxidation pathways contribute strongly. The stronger inhibition observed with methanol (MeOH; 23.2–25.8% under UV-A+PMS and 26.4–29.9% under visible light + PMS) relative to TBA is consistent with an additional sulfate-radical-type contribution under PMS activation, because MeOH can intercept both $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ in common mechanistic interpretations. These comparisons should still be treated as indicative rather than strictly diagnostic: scavenger tests report net kinetic impact and can be

influenced by adsorption to fibrous solids, changes in solution properties, and incomplete interception of short-lived species [76]. Even with these caveats, the pronounced suppression by TBA and MeOH under both irradiation modes supports that $\bullet\text{OH}$ -accessible radical oxidation is the dominant route to SMX disappearance in the TiO_2/BiOI -PMS system, with sulfate-radical-type chemistry plausibly contributing in parallel. The p-BQ causes only moderate inhibition (82.3–85.7% under UV-A + PMS; 84.8–89.2% under visible light + PMS), which is consistent with $\text{O}_2^{\bullet-}$ playing a secondary role relative to the $\bullet\text{OH}/\text{SO}_4^{\bullet-}$ manifold. Because p-BQ can also act as an electron acceptor, its effect cannot be interpreted as uniquely selective for $\text{O}_2^{\bullet-}$, but the limited inhibition aligns with $\text{O}_2^{\bullet-}$ being contributory rather than rate-determining under the PMS-assisted conditions tested. The impacts of charge-carrier scavengers are also moderate. EDTA decreased SMX degradation to 79.8–80.3% under UV-A + PMS and 82.4–85.3% under visible light + PMS, while AgNO_3 decreased degradation to 90.1–92.3% and 86.9–88.7%, respectively. These limited inhibitions indicate that free holes and long-lived electrons are not the sole rate-controlling oxidizing or reducing species responsible for SMX degradation. Instead, photo-generated carriers are more likely involved as short-lived initiators of interfacial PMS and dissolved-oxygen activation. In the TiO_2/BiOI /PMS system, $\bullet\text{OH}$ -accessible oxidative flux can arise through several coupled routes, including oxidation of surface hydroxyl groups or water by photogenerated holes, one-electron PMS activation at photoexcited semiconductor sites, conversion of $\text{SO}_4^{\bullet-}$ -type species into $\bullet\text{OH}$ through reaction with water or hydroxide, and secondary oxygen-derived pathways involving $\text{O}_2^{\bullet-}/\text{H}_2\text{O}_2$ -type intermediates. The moderate effects of EDTA and AgNO_3 therefore support carrier involvement in ROS initiation, but they do not identify a single dominant elementary step. Accordingly, the scavenger results are interpreted as evidence for a radical-accessible oxidation network rather than as proof of a purely direct hole- or electron-driven pathway. FFA produces only small changes relative to the no-quencher case (typically $\leq 15\%$ absolute decrease, and $< 10\%$ under visible light + PMS for TBO3), suggesting that $^1\text{O}_2$ is not the principal oxidant controlling SMX disappearance under these operating conditions. This does not exclude $^1\text{O}_2$ formation, but it argues against a mechanism in which $^1\text{O}_2$ dominates the observed SMX removal kinetics.

The scavenger picture is reinforced by the PMS-consumption and Ce(III) probe assays ($[\text{Ce(III)}]_0 = 2.5 \text{ mM}$), which also clarify how oxidant generation evolves over extended times and differs between irradiation modes and between TBO2 and TBO3. PMS depletion after 2 h is much more advanced under UV-A + PMS ($[\text{PMS}]_{2\text{h}} = 0.48 \text{ mM}$ for TBO2; 0.36 mM for TBO3) than under visible light + PMS ($[\text{PMS}]_{2\text{h}} = 1.85 \text{ mM}$ for TBO2; 1.63 mM for TBO3), consistent with a faster overall PMS turnover under UV-A irradiation. The divergence persists at longer times: under UV-A + PMS, PMS is almost exhausted by 8 h ($[\text{PMS}]_{8\text{h}} = 0.07 \text{ mM}$ for TBO2; 0.04 mM for TBO3) and reaches complete consumption within 24 h for both samples, whereas under visible light + PMS a substantial PMS reservoir remains at 8 h ($[\text{PMS}]_{8\text{h}} = 0.85 \text{ mM}$ for TBO2; 0.55 mM for TBO3) and is only partially depleted after 24 h ($[\text{PMS}]_{24\text{h}} = 0.22 \text{ mM}$ for TBO2; 0.06 mM for TBO3). Thus, visible irradiation sustains PMS activation over a much longer time window, and TBO3 maintains consistently higher PMS consumption than TBO2 across the full 24 h, pointing to a higher steady oxidative throughput rather than a short-lived burst confined to the first hours.

Ce(IV) accumulation shows the same hierarchy and adds an important temporal dimension. After 2 h, Ce(IV) is already high under UV-A + PMS (1.78–1.93 mM) but markedly lower under visible light + PMS (0.58–0.84 mM), again indicating stronger early-stage oxidizing flux under UV-A irradiation. However, the visible-light system continues to build oxidizing equivalents over time: Ce(IV) increases from 0.58 to 1.54 mM for TBO2 and from 0.84 to 1.89 mM for TBO3 between 2 h and 8 h, and reaches 2.21–2.39 mM by 24 h. This gradual rise contrasts with the UV-A + PMS case, where Ce(IV) approaches a near-plateau by 24 h (2.32–2.36 mM) as PMS becomes depleted. Because the Ce(III)/Ce(IV)

assay is best viewed as an operational readout of net one-electron oxidizing capacity in PMS-containing systems rather than a selective fingerprint of $\text{SO}_4^{\bullet-}$, the absolute Ce(IV) values cannot be mapped uniquely onto a single ROS. Even so, the coupled trends – ongoing PMS consumption together with sustained Ce(IV) formation under visible irradiation – support that PMS activation and associated one-electron oxidation pathways persist well beyond the first few hours. In practical terms, this argues against a purely transient “initial activation” regime and instead indicates a sustained oxidant-generation capability, particularly for TBO3, which continues to convert PMS and accumulate Ce(IV) more rapidly than TBO2 over the entire 24 h period.

These extended-time results are mechanistically relevant in two ways. First, they provide a rationale for why PMS-assisted conditions can drive deep oxidation (and, in the SMX tests, near-complete mineralization): oxidant generation is not limited to an early-time pulse but can be maintained as long as PMS remains available. Second, they help interpret the scavenger outcome that suggests a sulfate-radical-type contribution in parallel with $\bullet\text{OH}$ -accessible pathways. If sulfate-radical-type chemistry were only significant during a short initial PMS activation window, one would expect the probe signals and PMS consumption to converge rapidly; instead, the progressive Ce(IV) buildup and the measurable PMS reservoir remaining under visible light up to 24 h indicate that PMS-derived oxidizing channels remain active over extended durations. Residual PMS concentration profiles were measured to assess oxidant utilisation during photocatalytic PMS activation. The PMS concentration-versus-time plots in Fig. 3j show progressive PMS consumption under both UV-A + PMS and visible light + PMS conditions. These profiles complement the Ce(III)/Ce(IV) assay: Ce(IV) accumulation reflects the build-up of oxidizing equivalents under the probe conditions, whereas residual PMS directly tracks the consumption of the added oxidant. PMS depletion should nevertheless not be interpreted alone as catalytic efficiency, because oxidant consumption may include both productive pathways leading to SMX/intermediate oxidation and non-productive PMS decomposition.

The hTPA readout after 2 h provides additional, but still non-exclusive, evidence for $\bullet\text{OH}$ -accessible oxidative chemistry. hTPA concentrations are 285–296 nM under UV-A + PMS and 344–376 nM under visible light + PMS, again higher for TBO3 than for TBO2. Because terephthalate-based assays can respond to strongly oxidative media through indirect routes and are sensitive to probe accessibility and competitive consumption, these values are most robustly interpreted as confirming that oxidation pathways capable of converting terephthalate operate under both irradiation modes and are more pronounced for TBO3 under visible light. Singlet oxygen was further probed using SOSG. The SOSG fluorescence signal recorded at 45 min increases from 28 to 34 a.u. under UV-A + PMS to 48–65 a.u. under visible light + PMS, and is higher for TBO3 than for TBO2 in both irradiation modes. Because SOSG is a probe assay rather than a direct speciation method, its response should be interpreted comparatively: the higher SOSG signal under visible light + PMS is consistent with an increased $^1\text{O}_2$ -associated oxidative contribution under visible irradiation, and the TBO3 > TBO2 trend suggests that the intermediate BiOI growth state that optimizes visible light + PMS SMX kinetics also favors higher SOSG response under the probe conditions. At the same time, the modest inhibition observed with FFA compared with the strong suppression by MeOH/TBA indicates that, even if $^1\text{O}_2$ is generated, it is unlikely to be the dominant channel controlling SMX disappearance under the tested PMS-assisted conditions.

Taken together, the quenching and probe datasets support a radical-accessible PMS-assisted oxidation network rather than a single-ROS mechanism or definitive ROS speciation. The strong inhibition by TBA and MeOH is consistent with a major contribution from $\bullet\text{OH}$ -accessible oxidation pathways, while the stronger suppression by MeOH than by TBA suggests that sulfate-radical-type chemistry may contribute in parallel. This interpretation remains operational because MeOH/TBA comparisons alone cannot unambiguously prove $\text{SO}_4^{\bullet-}$ formation in

heterogeneous PMS systems, particularly when endpoint scavenger tests are performed with 1 mM scavenger in the presence of 2.5 mM PMS. The h-TPA response supports the presence of $\bullet\text{OH}$ -associated oxidative flux, while SOSG indicates a measurable $^1\text{O}_2$ -associated probe response; however, these assays are not absolute ROS quantification methods. Moreover, DMPO-based EPR would not, by itself, provide unambiguous $\text{SO}_4^{\bullet-}/\bullet\text{OH}$ discrimination in PMS systems. The DMPO- $\text{SO}_4^{\bullet-}$ adduct is short-lived and can hydrolyze or transform into DMPO-OH, while DMPO-OH signals may arise from direct $\bullet\text{OH}$ trapping, secondary conversion of sulfate-radical adducts, or oxidative artefacts involving PMS, DMPO, or the spin adducts. Therefore, a DMPO-OH signal alone cannot be taken as definitive proof of free $\bullet\text{OH}$, and a weak or absent DMPO- $\text{SO}_4^{\bullet-}$ signal would not exclude sulfate-radical-type chemistry.

Alternative spin traps such as DEPMPO or BMPO can improve adduct persistence in some systems, but they still require careful control experiments and do not remove all ambiguities in strongly oxidative PMS media. TEMP/TEMPOL-based approaches for $^1\text{O}_2$ also require dedicated controls because TEMP oxidation can be promoted by strongly oxidizing AOP conditions. Accordingly, the ROS assignments are presented as data-consistent pathways rather than definitive radical identification.

The TiO_2/BiOI interface can be rationalized within a p-n heterojunction framework. TiO_2 is generally considered an n-type semiconductor, whereas BiOI behaves as a p-type semiconductor. Upon intimate contact between both phases during solvothermal growth, equilibration of the Fermi levels is expected to induce interfacial band bending and generate an internal electric field across the TiO_2/BiOI

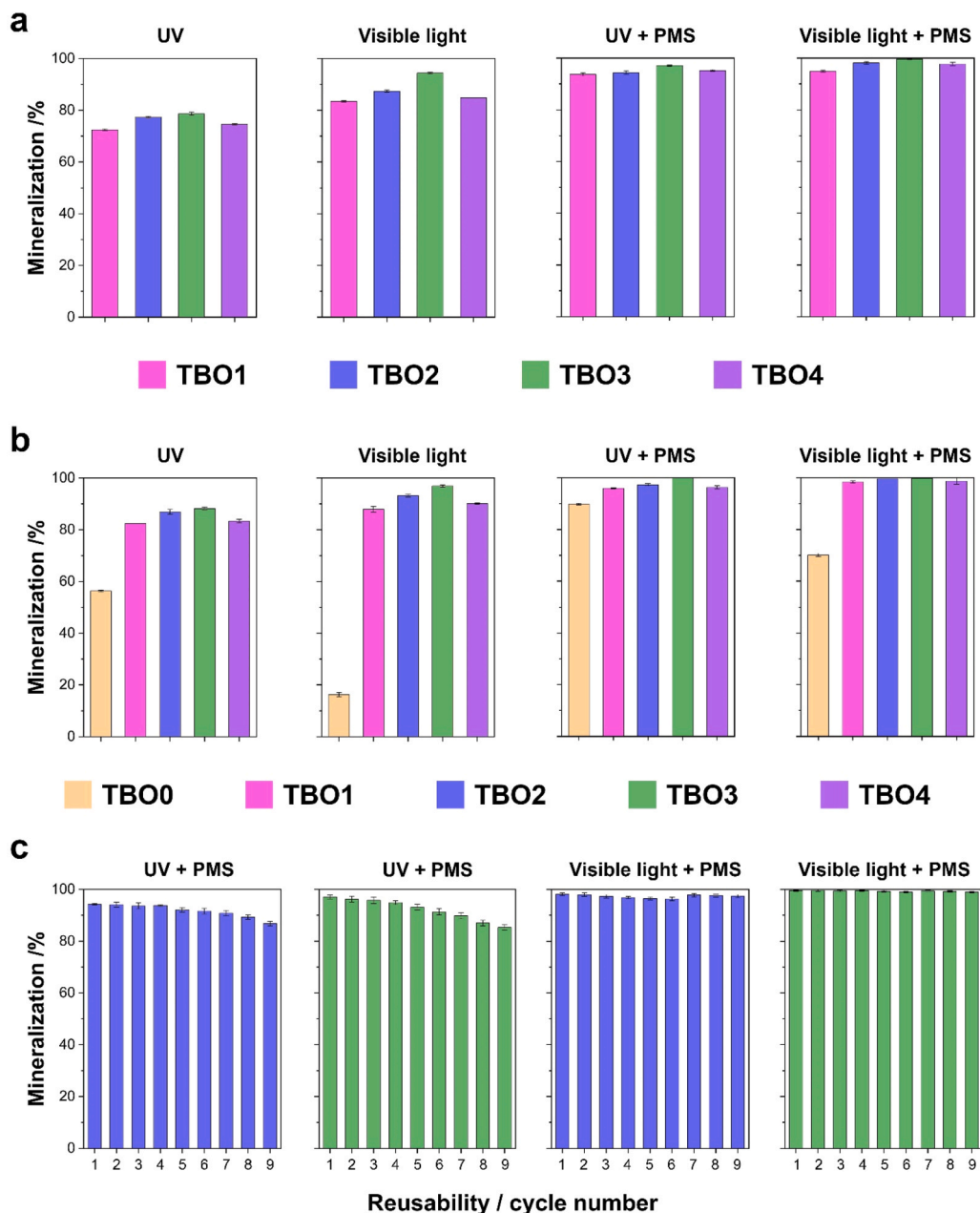


Fig. 4. TOC-based mineralization of the multi-pollutant (MP) solution (SMX, TC, LEV, and LAN) over hierarchical electrospun TiO_2/BiOI nanofibers with different BiOI growth states (TBO1–TBO4). (a) Mineralization (%) under UV-A or visible-light irradiation, in the absence and presence of PMS (2.5 mM), quantified from TOC removal at the end of the reaction. (b) Mineralization of the MP solution prepared in filtered tap water under the same irradiation and PMS conditions; TBO0 denotes pristine TiO_2 nanofibers. (c) Reusability of the best-performing catalysts (TBO2 and TBO3) over nine consecutive cycles under PMS-assisted irradiation (UV-A + PMS and visible light + PMS); after each run, the catalyst was recovered by centrifugation and rinsed four times with Milli-Q water before reuse in a fresh MP solution. Error bars represent mean $\pm$ standard deviation ($n = 3$).

junction. Similar p–n heterojunction effects have been reported for other coupled semiconductor systems, where the internal electric field facilitates charge separation and improves photocatalytic performance [77–79]. In the present TiO_2/BiOI fibers, this interfacial field may assist the spatial separation of photogenerated carriers and reduce recombination, consistent with the PL quenching trend and the enhanced visible-light activity observed for the optimally coated samples. Under irradiation, BiOI extends light absorption into the visible region, while TiO_2 contributes to the fibrous scaffold, interfacial contact, and UV-A response. The separated carriers generated at the TiO_2/BiOI interface can initiate PMS and dissolved-oxygen activation at surface sites. Photogenerated electrons may promote one-electron PMS activation to produce sulfate-radical-type oxidizing species and may also reduce dissolved O_2 to $\text{O}_2^{\bullet-}$ -related intermediates. In parallel, photogenerated holes can oxidize surface hydroxyl groups or water, contributing to $\bullet\text{OH}$ -accessible oxidative pathways. Subsequent conversion of sulfate-radical-type species by reaction with water or hydroxide may further contribute to $\bullet\text{OH}$ formation. This coupled p–n heterojunction/PMS activation pathway is consistent with the strong inhibition by TBA and MeOH, the PMS-consumption profiles, Ce(III) oxidation, and hTPA/SOSG probe responses.

TOC removal from the MP mixture provides a stringent metric because it integrates the fate of four chemically distinct organics (SMX, TC, LEV, and LAN) and therefore reflects the net balance between fast primary transformation and the slower, oxidative steps required to convert intermediates into carbon dioxide and inorganic ions [80,81] (Fig. 4a and Table S6). Under irradiation without PMS, the TiO_2/BiOI series already achieves substantial mineralization, with a clear dependence on illumination wavelength and BiOI growth state. Under UV-A irradiation without PMS, mineralization remains lower and less differentiated across the series ($72.4 \pm 0.3\%$ – $78.6 \pm 0.6\%$). TBO2 and TBO3 provide the highest TOC removal ($77.4 \pm 0.3\%$ and $78.6 \pm 0.6\%$, respectively), but the spread across TBO1–TBO4 is modest compared with the visible-light case. Under visible light, TOC removal increases from $83.5 \pm 0.3\%$ (TBO1) to $87.4 \pm 0.4\%$ (TBO2) and reaches a maximum of $94.4 \pm 0.3\%$ for TBO3, before decreasing to $84.8 \pm 0.0\%$ for TBO4. The non-monotonic trend (TBO3 > TBO4) mirrors the performance optimum observed in the SMX tests under visible irradiation and is consistent with an architectural/compositional trade-off: intermediate BiOI growth appears to provide sufficient visible-light harvesting and interfacial activity while preserving accessibility within the fibrous network, whereas further overgrowth can plausibly reduce adsorption-accessible surface and/or impose transport and optical-density penalties that are not compensated by additional BiOI loading. This smaller sensitivity is consistent with UV-A excitation accessing TiO_2 directly across all samples; in that regime, differences in the extent of BiOI overgrowth may matter less for photon absorption than they do under visible irradiation, and the overall mineralization may be limited more by the oxidative strength/flux available to drive late-stage intermediate oxidation than by initial light harvesting.

Adding PMS shifts the system toward near-quantitative mineralization under both wavelengths and compresses the performance gap among catalysts, while still preserving an advantage for TBO3. Under visible light + PMS, TOC removal increases to $94.8 \pm 0.4\%$ (TBO1), $98.1 \pm 0.4\%$ (TBO2), $99.5 \pm 0.2\%$ (TBO3), and $97.7 \pm 0.6\%$ (TBO4). Under UV-A + PMS, mineralization likewise rises to $93.6 \pm 0.6\%$ (TBO1), $94.3 \pm 0.6\%$ (TBO2), $97.1 \pm 0.3\%$ (TBO3), and $95.1 \pm 0.3\%$ (TBO4). Two points are worth emphasizing. First, PMS is decisive for deep oxidation of the MP solutions, bringing TOC removal into the mid-to-high 90% range even where irradiation alone is less effective, which is consistent with PMS activation supplying additional oxidative equivalents needed to process refractory intermediates generated from multiple parent compounds. Second, the best-performing catalyst under PMS-assisted operation remains TBO3 under both UV-A and visible illumination, suggesting that the intermediate-growth “hairy/cocoon-like” architecture offers a favorable balance between interfacial activity

and accessibility. The fact that visible light + PMS reaches slightly higher mineralization than UV-A + PMS for TBO2–TBO4 should not be over-interpreted as a wavelength effect per se without matched photon-flux/absorbed-photon analysis; however, it is at least consistent with the material design objective – enhanced visible-light utilization – being translated into strong PMS-assisted oxidative capacity under visible irradiation. Because TOC removal is a bulk endpoint that does not discriminate between adsorption, partial oxidation, and complete mineralization pathways, these MP results are best interpreted as comparative evidence of net oxidative throughput under each condition rather than as direct proof of a unique ROS identity or a single rate-limiting step. Even so, the tight standard deviations ($\leq 0.6\%$) and the systematic trends across conditions support a robust conclusion: PMS addition reliably drives the system toward near-complete mineralization of a complex MP solution, and the catalyst architecture tuned at intermediate solvothermal time (TBO3) provides the most effective platform for sustained deep oxidation under both UV-A and visible irradiation.

The robustness of the TiO_2/BiOI series was further evaluated using the four-component multipollutant solution prepared in filtered tap water (Fig. 4b and Table S7). This matrix contained relevant inorganic constituents, including bicarbonate, chloride, nitrate, hardness ions, alkalinity, and residual free chlorine, which can affect PMS activation by scavenging reactive species, modifying radical speciation, or altering pollutant–catalyst interactions. Despite this more complex background, the TiO_2/BiOI catalysts retained high mineralization activity. Under visible light without PMS, TOC removal increased from $16.3 \pm 0.8\%$ for pristine TiO_2 to $87.9 \pm 1.1\%$, $93.2 \pm 0.6\%$, $96.9 \pm 0.4\%$, and $90.1 \pm 0.3\%$ for TBO1–TBO4, respectively. Upon PMS addition, visible-light mineralization increased to $98.4 \pm 0.4\%$ for TBO1, $\geq 99.0\%$ for TBO2, $\geq 99.0\%$ for TBO3, and $98.7 \pm 1.2\%$ for TBO4, whereas pristine TiO_2 reached $70.2 \pm 0.6\%$. Under UV-A + PMS, the same trend was observed, with TBO3 reaching $\geq 99.0\%$ TOC removal. These results indicate that the hierarchical TiO_2/BiOI architecture remains active in the presence of common inorganic water-matrix constituents and that PMS-assisted operation preserves high oxidative depth under filtered tap-water conditions. Nevertheless, filtered tap water should be regarded as an intermediate matrix test rather than a full wastewater validation, because municipal wastewater would introduce additional variability, natural organic matter, suspended solids, ammonia, and other oxidant-demanding species.

3.2.1.1. Reusability and photostability of bioinspired hierarchical electrospun TiO_2/BiOI nanofibers. Catalyst durability was evaluated over nine consecutive cycles for TBO2 and TBO3 under PMS-assisted irradiation (UV-A+PMS and visible light + PMS) using the MP solution (Fig. 4c) [82]. Between cycles, the catalyst was recovered by centrifugation and rinsed four times with Milli-Q water before reuse in a fresh MP solution. No MP solution was used for washing, and no chemical or thermal regeneration treatment was applied. Therefore, the cycling experiment evaluates operational reuse after simple water rinsing and avoids intentional preloading of the catalyst surface with fresh organic pollutants between cycles.

Under UV-A + PMS, mineralization decreases beyond the reported uncertainty band, indicating measurable deactivation upon reuse. TBO2 drops from 94.3% to 86.8% by cycle 9 (–7.5 loss), while TBO3 decreases from 97.1% to 85.3% (–11.8 decrease). Although both catalysts remain highly active after nine cycles (>85% mineralization), the magnitude and systematic nature of the decline are too large to be attributed to ± 0.6 – 0.8% variability alone, showing that the UV-A + PMS environment imposes a stronger stability challenge. Under visible light + PMS, both catalysts maintain near-quantitative mineralization throughout cycling. TBO2 changes from 98.1% (cycle 1) to 97.4% (cycle 9) (–0.7 decrease), and TBO3 from 99.5% to 98.9% (–0.6 loss). Because the experimental variability is ~ 0.6 – 0.8% (absolute), these differences are within the uncertainty of the TOC-based mineralization measurement

and therefore indicate no statistically meaningful loss of activity under visible-light-driven PMS activation over nine runs. Minor non-monotonic fluctuations across intermediate cycles are consistent with routine run-to-run variability associated with catalyst recovery/handling and TOC analysis rather than progressive deactivation. Because the catalyst was rinsed with Milli-Q water rather than with MP solution, the observed TOC removal in each cycle cannot be attributed to pre-adsorption of fresh pollutants during the washing step. Strongly adsorbed residues or intermediates from previous cycles may still contribute to gradual surface fouling, but this effect is part of the operational stability assessment and would not artificially enhance the initial TOC removal of the following cycle through pollutant preloading.

Note that the different cycling behavior under UV-A + PMS and visible light + PMS is consistent with distinct PMS-activation regimes. Under UV-A irradiation, PMS is consumed much more rapidly, with residual PMS decreasing to 0.48 mM for TBO2 and 0.36 mM for TBO3 after 2 h. Under visible-light irradiation, residual PMS remains higher at the same time point, 1.85 mM for TBO2 and 1.63 mM for TBO3, indicating a more gradual oxidant-generation profile. The UV-A + PMS condition therefore imposes a stronger early oxidative stress on the catalyst, combining direct TiO_2 excitation, BiOI excitation, PMS activation, and rapid formation of oxidizing equivalents. This more aggressive environment can promote surface reconstruction and partial BiOI destabilization, consistent with the larger activity loss and ppb-level leaching observed after cycling. By contrast, visible-light irradiation mainly exploits the BiOI-containing heterostructure and sustains PMS activation more gradually, allowing high TOC removal while limiting photochemical damage to the catalyst surface. This comparison should not be interpreted as evidence that visible-light excitation is intrinsically more stable under all conditions. Photon fluxes and absorbed photon numbers were not normalized between the UV-A and visible-light experiments. The higher cyclability under visible light + PMS is therefore best described as an operational stability advantage under the tested conditions, arising from a less abrupt PMS-activation regime and reduced photocorrosive stress on the TiO_2/BiOI system.

Post-run characterization supports structural and surface robustness at the levels probed. FE-SEM images after nine cycles show minimal morphological changes (Figure S2), suggesting that the fibrous architecture is retained at the microscale. XPS spectra collected before and after cycling show no obvious changes in surface chemical features within the resolution and sampling depth of XPS (Figure S3), arguing against major surface reconstruction or complete loss of the BiOI component at the outer surface. Leaching tests nevertheless reveal a clear irradiation-mode dependence: under UV-A + PMS, Ti, Bi, and I are detected in solution at the ppb level, whereas under visible light + PMS these elements are below detection. Post-run characterization supports structural and surface robustness at the levels probed. FE-SEM images after nine cycles show minimal morphological changes (Figure S2), suggesting that the fibrous architecture is retained at the microscale. XPS spectra collected before and after cycling show no obvious the main Ti, Bi, I, and O surface features within the resolution and sampling depth of XPS (Figure S3), arguing against severe surface reconstruction or complete loss of the BiOI component at the outer surface. Leaching tests nevertheless reveal a clear irradiation-mode dependence: under UV-A + PMS, Ti, Bi, and I are detected in solution at the ppb level, whereas under visible light + PMS these elements are below detection. The stability data should be interpreted in relation to the sensitivity of each characterization method. The combined FE-SEM/XPS/leaching evidence supports retention of the gross fibrous architecture and surface chemical signatures, but it does not by itself demonstrate complete crystallographic or textural invariance after cycling. The larger activity loss observed under UV-A + PMS is therefore attributed cautiously to a harsher oxidative regime that may promote surface-localized BiOI alteration, partial iodine depletion, low-level leaching, and/or active-site passivation, rather than to complete destruction of the TiO_2/BiOI architecture. Overall, the cycling results indicate high operational

reusability under visible light + PMS and a gradual, measurable decline under UV-A + PMS, while the combined FE-SEM/XPS/leaching evidence supports retention of the gross architecture and surface signatures within the sensitivity of the techniques used.

3.2.1.2. Biototoxicity assessment of treated water. The phytotoxicity of untreated and treated waters was evaluated using a *Lactuca sativa* seed germination and early root-growth inhibition assay, with outcomes expressed as relative germination (RG), relative root elongation (RRE), and the germination index (GI) [83,84]. Representative images of seeds after 5 days of incubation (dark, 20 °C, humid chambers) are shown in Fig. 5 for the untreated MP solution and for MP solutions treated for 2 h using TBO2 or TBO3 under visible irradiation, either without PMS or with PMS. Because PMS can impose direct oxidative stress during the bioassay, PMS-treated samples were quenched with $\text{Na}_2\text{S}_2\text{O}_3$ (0.5 M) prior to germination testing, to minimize continued oxidant action during incubation.

The untreated MP solution strongly inhibited both germination and early root development, yielding $\text{RG} \approx 62.5\%$, $\text{RRE} \approx 17.2\%$, and $\text{GI} \approx 10.8\%$, well below the $\text{GI} < 50\%$ criterion typically used to indicate high phytotoxicity in this screening assay. In addition, the PMS-only control led to complete suppression of germination under the conditions tested (Fig. 5c), highlighting that PMS cannot be dosed directly into receiving waters without an activation/neutralization strategy and that any residual oxidant must be effectively quenched prior to downstream reuse or biological contact.

In contrast, photocatalytically treated MP waters showed substantially improved germination and root growth, with GI values shifting into the moderate-to-low phytotoxicity ranges depending on catalyst and PMS addition. When TBO2 was used under visible irradiation, the treated water gave $\text{RG} \approx 89.8\%$, $\text{RRE} \approx 87.4\%$, and $\text{GI} \approx 78.6\%$, i.e., near the boundary between moderate (50–80%) and low (>80%) phytotoxicity. Adding PMS during treatment with TBO2 further improved the bioassay response to $\text{RG} \approx 95.6\%$, $\text{RRE} \approx 122.4\%$, and $\text{GI} \approx 117.1\%$, consistent with a strong reduction of the biologically inhibiting load after PMS-assisted oxidation. For TBO3, visible-light treatment also yielded a low-phytotoxicity effluent: $\text{RG} \approx 99.9\%$ and $\text{GI} \approx 103\%$ (corresponding to $\text{RRE} \approx 103\%$ by the GI definition). Under visible light + PMS with TBO3, the effluent similarly remained in the low-phytotoxicity regime ($\text{RG} \approx 87.5\%$, $\text{RRE} \approx 131.5\%$, $\text{GI} \approx 115.0\%$).

GI values exceeding 100% are sometimes interpreted as “stimulation” (hormesis) relative to the Milli-Q control; however, such responses should be interpreted cautiously in photocatalytic AOP effluents. Apart from biological variability, matrix effects can contribute, including changes in ionic composition after oxidation/mineralization (e.g., inorganic ions produced from the parent compounds and/or from PMS-derived sulfate) and any residual quenching products, which can alter osmotic conditions or act as nutrients that influence early root elongation [26]. Accordingly, the most robust conclusion from these data is comparative: visible-light photocatalysis with TiO_2/BiOI substantially mitigates the severe phytotoxicity of the untreated MP solution, and PMS-assisted operation (when catalytically activated and quenched prior to testing) yields consistently low-phytotoxicity effluents in this screening assay, in line with the high mineralization levels observed for the same treatment conditions.

3.2.2. Microplastic degradation

Cross-linked PS microparticles (10 μm ; 2% cross-linking) were selected as a stringent microplastic model because the covalent network limits swelling and chain mobility, which typically slows oxidative breakdown under mild conditions [85,86]. In this context, time-resolved FE-SEM offers a sensitive way to distinguish physical aggregation (e.g., necking/coalescence) from chemical degradation signatures (surface oxidation, embrittlement, delamination, and fragmentation) that are consistent with polymer-chain scission. All microplastic experiments

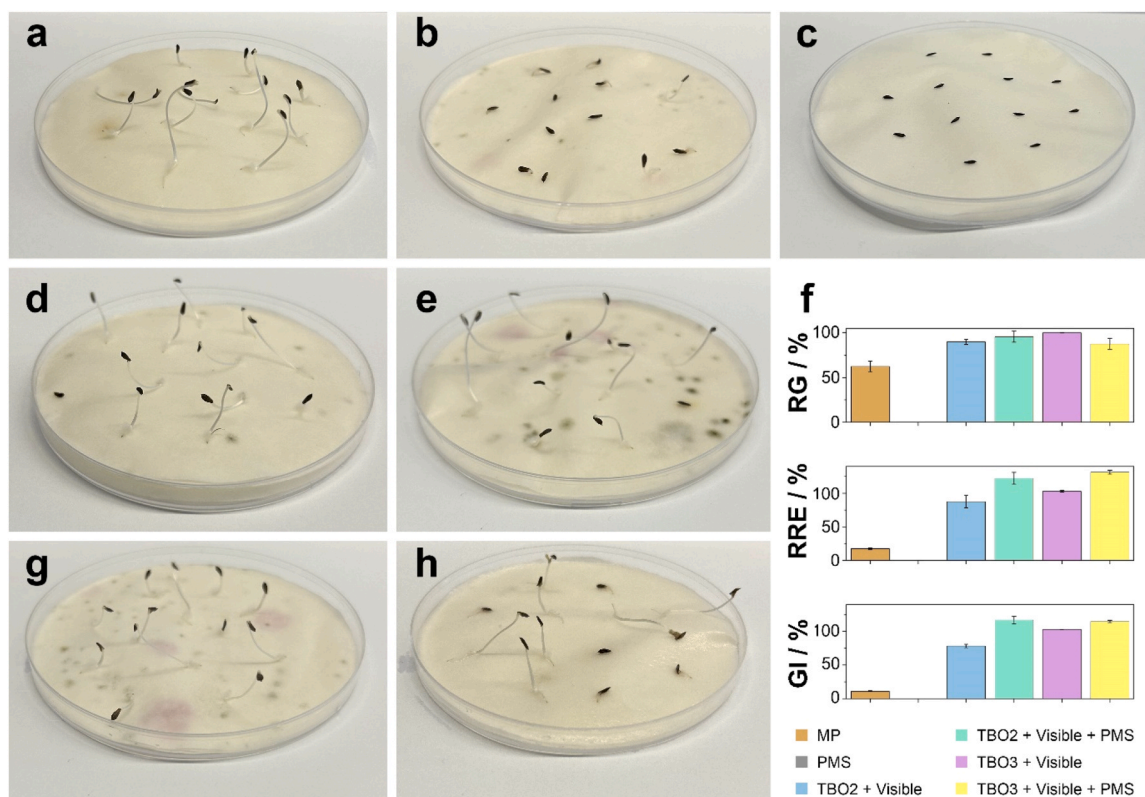


Fig. 5. Phytotoxicity assessment of untreated and treated multipollutant (MP) solutions using lettuce (*Lactuca sativa*) seed germination and root elongation assays. Representative photographs after 5 days of incubation for seeds exposed to (a) Milli-Q water control, (b) untreated MP solution, (c) PMS control, (d) TBO2 + visible, (e) TBO2 + visible + PMS, (g) TBO3 + visible, and (h) TBO3 + visible + PMS. (f) Relative germination (RG), relative root elongation (RRE), and germination index (GI), calculated relative to the Milli-Q water control. Twelve lettuce seeds were used per Petri dish, and assays were performed in triplicate. Error bars represent mean $\pm$ standard deviation.

were performed at $[PS]_0 = 20$ ppm (solids) and $[PMS]_0 = 2.5$ mM under visible irradiation (465–470 nm), comparing TBO2 and TBO3 (1.0 mg mL^{-1}) against catalyst-free controls (Figure S3).

When PS was contacted with PMS for 24 h in the dark (i.e., without photoactivation), no measurable changes in particle size, surface roughness, or packing were observed (Figure S3a). This outcome is mechanistically expected: at near-neutral conditions PMS is not sufficiently reactive toward the chemically inert PS backbone unless it is efficiently activated to generate short-lived, highly oxidizing species. By contrast, visible irradiation alone for 24 h (no PMS, no catalyst) did not produce erosion or fragmentation, but it did promote lateral particle–particle joining (“bridges”/necks) and the appearance of clusters larger than the nominal particle diameter (Figure S3b). This necking behavior is characteristic of surface softening and increased tackiness at contact points (e.g., weak photo-oxidation and/or local thermal-assisted surface rearrangement), which strengthens interparticle adhesion and drives irreversible aggregation. Importantly, these controls indicate that PMS alone is ineffective without activation, and light alone mainly modifies interparticle interactions, not polymer integrity.

Under visible-light irradiation and PMS in presence of $TiO_2/BiOI$ catalysts, FE-SEM reveals a coherent progression from intact spheres to oxidized shells, delamination, and extensive fragmentation (Fig. 6). The transformation is not a simple size decrease; instead, it matches the expected behavior for surface-dominated oxidation of a cross-linked polymer, where attack initiates at the particle exterior, produces a mechanically weakened “skin,” and then advances inward as the shell fails and sheds debris [87,88].

Pristine PS appears as smooth, well-defined spheres with no evidence of erosion (Fig. 6a). With TBO2, the earliest changes at 2 h include localized roughening, microcracks, and an altered surface “skin” on

some spheres, while others remain comparatively smooth (Fig. 6b), consistent with heterogeneous initiation at catalyst–particle contact regions and locally higher ROS flux. At 4 h, the emergence of lamellar/petal-like features and folded structures indicates that the oxidized outer layer becomes brittle and begins to detach (delamination/peeling), forming rosette-like morphologies consistent with collapse/folding of a thin detached skin (Fig. 6c). By 6 h, many particles lose spherical integrity and appear as cup-like shells and fractured remnants, accompanied by an increased amount of small fragments (Fig. 6d), which is typical of an “outside-in” degradation mode culminating in shell failure. After 24 h, fragmentation dominates, with abundant lamellar shards and fine debris (Fig. 6e), consistent with sustained oxidative chain scission and repeated mechanical failure of the cross-linked network. With TBO3, the same qualitative trajectory is observed, but the delamination/fragmentation signature is more pronounced. At 2 h, the coexistence of relatively smooth spheres with strongly attacked, wrinkled/porous surfaces highlights marked spatial heterogeneity (Fig. 6f), plausibly arising from local catalyst distribution and microenvironments controlling PMS activation and ROS availability. At 4–6 h (Figs. 6g and 6h), rosette-like extrusions and large “flower” morphologies become prominent, consistent with extensive delamination and collapse of an oxidized shell, alongside substantial microdebris. After 24 h, the field is dominated by lamellar fragments and aggregated rosette remnants (Fig. 6i), indicating advanced erosion and fragmentation.

Across both catalysts, the particles evolve through a consistent sequence: smooth spheres $\rightarrow$ roughened/cracked oxidized skin $\rightarrow$ delamination into rosettes/lamellae $\rightarrow$ shell collapse $\rightarrow$ abundant fragments and debris.

The observed degradation is consistent with visible-light excitation of the $TiO_2/BiOI$ heterostructure generating charge carriers that

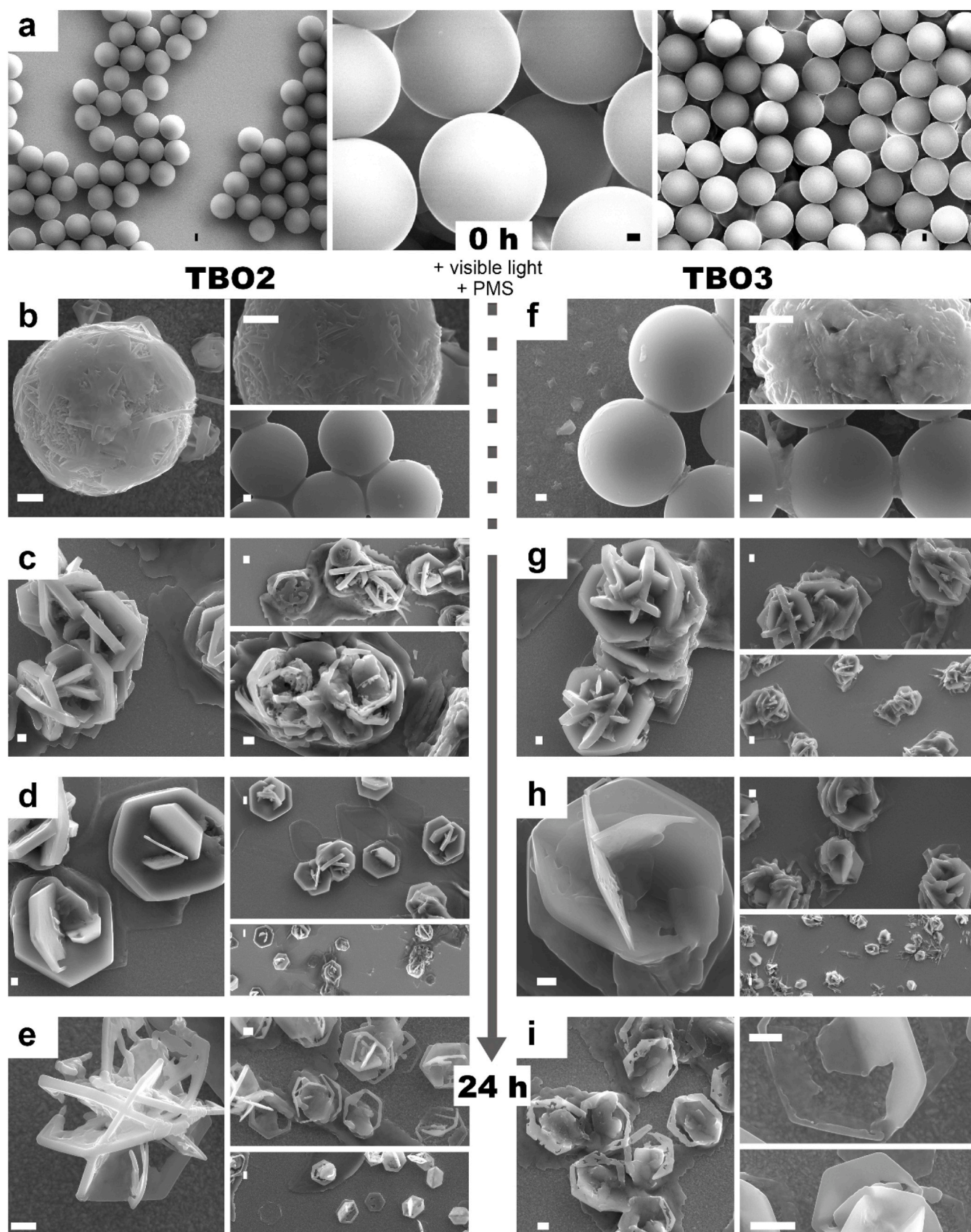


Fig. 6. FE-SEM micrographs of cross-linked polystyrene (PS) microparticles and their degradation under visible-light irradiation in the presence of PMS (2.5 mM). (a) Pristine PS microparticles (mean diameter 10 μm ; standard deviation $<0.2 \mu\text{m}$). Time-resolved degradation in the PS/PMS system using 1.0 mg mL^{-1} of TBO2 after (b) 2 h, (c) 4 h, (d) 6 h, and (e) 24 h. Time-resolved degradation in the PS/PMS system using 1.0 mg mL^{-1} of TBO3 after (f) 2 h, (g) 4 h, (h) 6 h, and (i) 24 h. Scale bar: 1 μm . $[\text{PS}]_0 = 20 \text{ ppm}$, $[\text{PMS}]_0 = 2.5 \text{ mM}$, catalyst dose: 1 mg mL^{-1} .

promote interfacial PMS activation, producing a sustained oxidative environment dominated by PMS-derived radical pathways (commonly $\text{SO}_4^{\bullet-}$, with secondary $\bullet\text{OH}$ formed downstream, and potentially additional oxygen-derived species depending on conditions). These oxidants can degrade PS through: (i) H-abstraction to form polymer radicals, (ii) oxygen incorporation (increasing polarity and disrupting packing), (iii) chain scission that lowers molecular weight and mechanical integrity, and (iv) embrittlement/delamination of an oxidized surface layer, yielding the characteristic rosette/lamellar morphologies followed by fragmentation into shards and fine debris. This framework also rationalizes the controls: PMS alone lacks an efficient activation route and shows negligible impact, while light alone promotes necking/aggregation but not oxidative erosion; only visible light + catalyst + PMS produces the characteristic erosion/delamination/fragmentation trajectory.

To complement the FE-SEM observations, larger-volume experiments were performed after 24 h to obtain an operational estimate of polymer fragmentation and transfer into the aqueous/sub-10 μm fraction. The initial 1.0 mL experiments were used only for morphological assessment, whereas the scaled-up 250 mL suspensions allowed TOC and gravimetric analysis after filtration through a 10.0 μm membrane, which retained the TiO_2/BiOI fibers and residual micrometer-sized PS particles. Under this separation protocol, the recoverable micrometer-sized particulate fraction decreased by 67% for TBO2 and 84% for TBO3. Catalyst-only controls processed in the absence of PS showed no appreciable TiO_2/BiOI fibers or catalyst fragments in the dried filtrates by FE-SEM, indicating negligible catalyst carry-over through the filter within the limits of the analysis. The decrease in the recoverable particulate fraction is therefore consistent with oxidative fragmentation, partial solubilization, and transfer of polymer-derived carbonaceous material into dissolved, colloidal, or sub-10 μm forms during treatment. The stronger effect observed for TBO3 agrees with the more advanced cracking, delamination, and fragmentation seen by FE-SEM and with sustained PMS-assisted oxidative activity under visible-light irradiation. These values should be interpreted as operational indicators of PS fragmentation/solubilization rather than as a complete polymer mass balance; full carbon closure would require independent quantification of retained particles, dissolved organic carbon, submicrometric fragments, volatile products, and mineralized carbon.

4. Conclusions

Persistent antibiotics and microplastics remain challenging targets for conventional treatment trains because they combine low biodegradability with high physicochemical stability; this study introduces bioinspired hierarchical electrospun TiO_2/BiOI nanofibers (TBO1–TBO4), tuned by solvothermal BiOI growth (2–16 h), as a multifunctional photocatalytic architecture for PMS activation that couples deep oxidation of dissolved pharmaceuticals with degradation of particulate microplastics.

Under neutral conditions (pH 7, 20 $^\circ\text{C}$; SMX 5 ppm; catalyst 0.50 g L^{-1} ; PMS 2.5 mM), PMS-assisted operation consistently drove near-complete mineralization under both UV-A (365 nm) and visible light (450 nm), whereas PMS alone (<8% SMX loss; <3% TOC removal at 120 min) and direct photolysis (<4% SMX loss) were negligible. In the absence of PMS, UV-A irradiation enabled substantial SMX conversion (59.5–80.8% at 80 min) but incomplete mineralization (62.5–79.2% TOC at 120 min), while visible irradiation yielded high SMX conversion (76.6–89.6% at 80 min) yet only moderate TOC removal (76.7–81.1% at 120 min), evidencing the persistence of oxidation-resistant intermediates without PMS. With PMS, the performance converged toward quantitative oxidation: under UV-A + PMS, SMX reached 92.9–98.1% conversion at 80 min with 96.5–98.8% TOC removal at 120 min ($k_{\text{obs}} = 1.1\text{--}7.3 \times 10^{-2} \text{ min}^{-1}$; maximum for TBO3), whereas visible light + PMS produced the clearest catalyst differentiation and an optimum at intermediate BiOI growth. Specifically, TBO3 showed near-

complete SMX mineralization after blank correction at 120 min with the fastest kinetics ($k_{\text{obs}} = 7.3 \times 10^{-2} \text{ min}^{-1}$; $t_{1/2} \approx 8.8 \text{ min}$), consistent with a trade-off between enhanced visible absorption and progressive masking of adsorption-accessible surface area at high BiOI coverage. This balance was reinforced by mineralization of a stringent four-component multipollutant solution (SMX/TC/LEV/LAN, 20 ppm total): without PMS, visible-light TOC removal peaked at $94.4 \pm 0.3\%$ for TBO3 (vs $83.5 \pm 0.3\%$ for TBO1 and $84.8 \pm 0.0\%$ for TBO4), while PMS raised mineralization to $94.8 \pm 0.4\text{--}99.5 \pm 0.2\%$ under visible light and $93.6 \pm 0.6\text{--}97.1 \pm 0.3\%$ under UV-A, with TBO3 remaining the top performer in both modes.

Mechanistic interrogation supports a radical-dominated PMS-assisted oxidation landscape sustained over extended times. Quenching tests showed strong inhibition by TBA ($\bullet\text{OH}$ -accessible pathways) and even stronger suppression by methanol, consistent with an additional sulfate-radical-type contribution; p-benzoquinone and furfuryl alcohol produced only moderate-to-minor effects, indicating secondary roles for $\text{O}_2^{\bullet-}$ -associated and $^1\text{O}_2$ -associated channels in controlling SMX disappearance. PMS depletion and Ce(IV) accumulation were consistent with sustained oxidant turnover under visible light + PMS over 24 h, with TBO3 showing higher PMS consumption and Ce(IV) formation than TBO2 under the probe conditions. Operationally, TBO2 and TBO3 maintained near-complete TOC removal of the MP solution over nine cycles under visible light + PMS ($\leq 0.7\%$ age-point change; Ti/Bi/I below detection), whereas UV-A + PMS caused measurable deactivation (to 86.8% for TBO2 and 85.3% for TBO3 by cycle 9) alongside ppb-level leaching. Detoxification tracked mineralization: the untreated MP solution was highly phytotoxic ($\text{GI} \approx 10.8$), while treated effluents under visible irradiation with TiO_2/BiOI shifted to low phytotoxicity (e.g., TBO3: $\text{GI} \approx 103$; TBO3 + PMS: $\text{GI} \approx 115$, with PMS quenched prior to testing).

Beyond dissolved pollutants, the system produced clear morphological and operational evidence of PS microplastic transformation under visible irradiation, where controls established that PMS in the dark caused no measurable changes and light alone primarily induced particle–particle necking without erosion. In contrast, cross-linked PS microparticles (10 μm ; 2% cross-linking; 20 ppm solids) exposed to visible light (465–470 nm) + PMS (2.5 mM) in the presence of TiO_2/BiOI (1.0 mg mL^{-1}) underwent a sequence of FE-SEM-observed changes consistent with outside-in oxidative damage captured by time-resolved FE-SEM: smooth spheres transitioned to roughened/cracked oxidized skins (2 h), followed by delamination into rosette/lamellar shells (4 h), shell collapse with fractured remnants (6 h), and fields dominated by lamellar shards and fine debris at 24 h. Scaled-up 24 h experiments further supported polymer fragmentation and solubilization, with the recoverable micrometre-sized particulate fraction decreasing by 67% for TBO2 and 84% for TBO3 under the applied filtration protocol. Catalyst-only controls indicated negligible TiO_2/BiOI carry-over through the 10.0 μm filter, supporting that the observed filtrate residue and TOC response mainly arise from polymer-derived products rather than catalyst leakage. These values should be interpreted as operational indicators of PS fragmentation and transfer into dissolved, colloidal, or sub-10 μm carbonaceous fractions, not as a complete polymer mass balance. The main limitations of the present work are the lower durability observed under UV-A + PMS and the unresolved carbon partitioning during microplastic transformation, including the relative contributions of retained particles, soluble/colloidal oxidation products, submicrometric fragments, and mineralized carbon. Future work should therefore focus on integrating hierarchical TiO_2/BiOI materials into recoverable visible-light reactor formats, improving long-term stability, reducing PMS demand, and closing the carbon balance for microplastic transformation in realistic water matrices.

CRediT authorship contribution statement

Mikhael Bechelany: Writing – review & editing, Supervision,

Project administration, Methodology, Funding acquisition, Conceptualization. **Elvira Gómez:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Albert Serrà:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Laura Huidobro:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Mahmoud Abid:** Writing – review & editing, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2026.123947](https://doi.org/10.1016/j.jece.2026.123947).

Data Availability

Data will be made available on request.

References

- [1] A. Atrashkevich, A. Alum, R. Stirling, M. Abbaszadegan, S. Garcia-Segura, Approaching easy water disinfection for all: can in situ electrochlorination outperform conventional chlorination under realistic conditions? *Water Res.* 250 (2024) 121014 <https://doi.org/10.1016/j.watres.2023.121014>.
- [2] M. Khmaissa, H. Zouari-Mechichi, G. Sciara, E. Record, T. Mechichi, Pollution from livestock farming antibiotics an emerging environmental and human health concern: A review, *J. Hazard. Mater. Adv.* 13 (2024) 100410, <https://doi.org/10.1016/j.hazadv.2024.100410>.
- [3] M. Ahmed, M.O. Mavukkandy, A. Giwa, M. Elektorowicz, E. Katsou, O. Khelifi, V. Naddeo, S.W. Hasan, Recent developments in hazardous pollutants removal from wastewater and water reuse within a circular economy, *Npj Clean. Water* 5 (2022) 12, <https://doi.org/10.1038/s41545-022-00154-5>.
- [4] M.S. De Ilurdoz, J.J. Sadhwani, J.V. Reboso, Antibiotic removal processes from water & wastewater for the protection of the aquatic environment - a review, *J. Water Process. Eng.* 45 (2022) 102474, <https://doi.org/10.1016/j.jwpe.2021.102474>.
- [5] R. Hernández-Tenorio, Degradation pathways of sulfamethoxazole under phototransformation processes: A data base of the major transformation products for their environmental monitoring, *Environ. Res.* 262 (2024) 119863, <https://doi.org/10.1016/j.envres.2024.119863>.
- [6] T.H. Le, T. Truong, L.-T. Tran, D.-H. Nguyen, T.P.T. Pham, C. Ng, Antibiotic resistance in the aquatic environments: the need for an interdisciplinary approach, *Int. J. Environ. Sci. Technol.* 20 (2023) 3395–3408, <https://doi.org/10.1007/s13762-022-04194-9>.
- [7] M. Zhuo, Z. Chen, X. Liu, W. Wei, Y. Shen, B.-J. Ni, A broad horizon for sustainable catalytic oxidation of microplastics, *Environ. Pollut.* 340 (2024) 122835, <https://doi.org/10.1016/j.envpol.2023.122835>.
- [8] A.G. Stancu, M. Răpă, C.L. Popa, S.I. Donțu, E. Matei, C.I. Covaliu-Mirelă, Degradation of emerging plastic pollutants from aquatic environments using TiO₂ and their composites in visible light photocatalysis, *Molecules* 30 (2025) 3186, <https://doi.org/10.3390/molecules30153186>.
- [9] Z. Bogart, A. Atrashkevich, J. Ananattarachai, S. Sinha, S. Garcia-Segura, P. Westerhoff, Towards low energy greywater treatment of surfactants and pathogens, *Discov. Water* 5 (2025) 96, <https://doi.org/10.1007/s43832-025-00295-x>.
- [10] E. Brillas, S. Garcia-Segura, Electrochemical advanced oxidation processes for real wastewater remediation: systems, performance, and generated oxidants, *ACS Electrochem.* 1 (2025) 2292–2316, <https://doi.org/10.1021/acselectrochem.5c00311>.
- [11] S. Zhang, H. Zheng, P.G. Tratnyek, Advanced redox processes for sustainable water treatment, *Nat. Water* 1 (2023) 666–681, <https://doi.org/10.1038/s44221-023-00098-1>.
- [12] S. Garcia-Segura, E. Brillas, Applied photoelectrocatalysis on the degradation of organic pollutants in wastewaters, *J. Photochem. Photobiol. C Photochem. Rev.* 31 (2017) 1–35, <https://doi.org/10.1016/j.jphotochemrev.2017.01.005>.
- [13] M.S. Gaber, S. Garcia-Segura, M.R.V. Lanza, A.J. Dos Santos, Enabling decentralized treatment of BPA through electrified photo-activated advanced oxidation, *Sep. Purif. Technol.* 382 (2026) 136095, <https://doi.org/10.1016/j.seppur.2025.136095>.
- [14] A. Serrà, E. Gómez, N. Al Hoda Al Bast, Y. Zhang, M. Duque, M. José Esplandiu, J. Esteve, J. Nogués, B. Sepúlveda, Wireless pulsed nanophotoelectrochemical cell for the ultrafast degradation of organic pollutants, *Chem. Eng. J.* 487 (2024) 150663, <https://doi.org/10.1016/j.cej.2024.150663>.
- [15] A. Saravanan, V.C. Deivayanai, P.S. Kumar, G. Rangasamy, R.V. Hemavathy, T. Harshana, N. Gayathri, K. Alagumalai, A detailed review on advanced oxidation process in treatment of wastewater: mechanism, challenges and future outlook, *Chemosphere* 308 (2022) 136524, <https://doi.org/10.1016/j.chemosphere.2022.136524>.
- [16] W. Lin, X. Liu, A. Ding, H.H. Ngo, R. Zhang, J. Nan, J. Ma, G. Li, Advanced oxidation processes (AOPs)-based sludge conditioning for enhanced sludge dewatering and micropollutants removal: A critical review, *J. Water Process. Eng.* 45 (2022) 102468, <https://doi.org/10.1016/j.jwpe.2021.102468>.
- [17] R. Montenegro-Ayo, T. Pérez, M.R.V. Lanza, E. Brillas, S. Garcia-Segura, A.J. Dos Santos, New electrochemical reactor design for emergent pollutants removal by electrochemical oxidation, *Electrochim. Acta* 458 (2023) 142551, <https://doi.org/10.1016/j.electacta.2023.142551>.
- [18] J. Liu, S. Zhang, W. Wang, H. Zhang, Photoelectrocatalytic principles for meaningfully studying photocatalyst properties and photocatalysis processes: From fundamental theory to environmental applications, *J. Energy Chem.* 86 (2023) 84–117, <https://doi.org/10.1016/j.jechem.2023.06.038>.
- [19] A. Aranda-Aguirre, D. Valdivia-Alvarez, E.C. Pastrana, S. Garcia-Segura, G. A. Cerrón-Calle, H. Alarcon, Engineered controlled on the synthesis of bismuth-molybdenum oxide semiconductors tailors photoelectrocatalytic activity, *J. Electroanal. Chem.* 980 (2025) 118956, <https://doi.org/10.1016/j.jelechem.2025.118956>.
- [20] S. Ali, P.M. Ismail, M. Khan, A. Dang, S. Ali, A. Zada, F. Raziq, I. Khan, M.S. Khan, M. Ateeq, W. Khan, S.H. Bakhtiar, H. Ali, X. Wu, M.I.A. Shah, A. Vinu, J. Yi, P. Xia, L. Qiao, Charge transfer in TiO₂-based photocatalysis: fundamental mechanisms to material strategies, *Nanoscale* 16 (2024) 4352–4377, <https://doi.org/10.1039/D3NR04534J>.
- [21] L. Huidobro, M. Allés, M. Abid, M. Bechelany, C. Sousa, E. Gómez, A. Serrà, Engineered SnO₂/BiOI fibers via electrospinning for robust visible-light/peroxymonosulfate-driven multipollutant mineralization, *Chem. Eng. J.* 531 (2026) 174316, <https://doi.org/10.1016/j.cej.2026.174316>.
- [22] Z. Honarmandrad, X. Sun, Z. Wang, M. Naushad, G. Boczkaj, Activated persulfate and peroxymonosulfate based advanced oxidation processes (AOPs) for antibiotics degradation – A review, *Water Resour. Ind.* 29 (2023) 100194, <https://doi.org/10.1016/j.wri.2022.100194>.
- [23] W. Zhao, Q. Shen, T. Nan, M. Zhou, Y. Xia, G. Hu, Q. Zheng, Y. Wu, T. Bian, T. Wei, C. Zhang, Cobalt-based catalysts for heterogeneous peroxymonosulfate (PMS) activation in degradation of organic contaminants: Recent advances and perspectives, *J. Alloy. Compd.* 958 (2023) 170370, <https://doi.org/10.1016/j.jallcom.2023.170370>.
- [24] L. Pang, Y. Liu, Z. Meng, A. Du, J. Gu, H. Liu, The activation mechanisms of permonosulfate and pollutant degradation pathways by generated reactive species, *Environ. Sci. Nano* 12 (2025) 5116–5145, <https://doi.org/10.1039/D5EN00675A>.
- [25] G.A. Cerrón-Calle, M. Flores, M.A. Roldan, K. Flores, E. Brillas, A.J. Dos Santos, S. Garcia-Segura, Electrochemical persulfate activation for degradation of BPA using a novel self-standing CuO_x/CoO_x cathode, *Chem. Eng. J.* 519 (2025) 164960, <https://doi.org/10.1016/j.cej.2025.164960>.
- [26] Q. Bautista, J. Rigual, J. Lloreda, A. Fons, J. Nogués, E. Gómez, B. Sepúlveda, A. Serrà, Synergistic photothermal/photocatalytic activation of peroxymonosulfate

- using SrFe₁₂O₁₉@Ni-P core@shell microparticles for energy efficient water remediation, *Chem. Eng. J.* 530 (2026) 173570, <https://doi.org/10.1016/j.cej.2026.173570>.
- [27] L. Huidobro, Q. Bautista, M. Alinezhadfar, E. Gómez, A. Serrà, Enhanced visible-light-driven peroxymonosulfate activation for antibiotic mineralization using electrosynthesized nanostructured bismuth oxyiodides thin films, *J. Environ. Chem. Eng.* 12 (2024) 112545, <https://doi.org/10.1016/j.jece.2024.112545>.
- [28] L. Huidobro, M. Abid, H. Maslouh, A. Demore, M. Bechelany, E. Gómez, A. Serrà, Atomic layer deposition of SnO₂ and TiO₂ on electrodeposited BiOI thin films for efficient light-driven peroxymonosulfate activation, *Mater. Des.* 257 (2025) 114375, <https://doi.org/10.1016/j.matdes.2025.114375>.
- [29] L. Huidobro, A. Domingo, E. Gómez, A. Serrà, Bismuth oxyiodide-based composites for advanced visible-light activation of peroxymonosulfate in pharmaceutical mineralization, *Chemosphere* 366 (2024) 143532, <https://doi.org/10.1016/j.chemosphere.2024.143532>.
- [30] E. Gómez, R. Cestaro, L. Philippe, A. Serrà, Electrodeposition of nanostructured Bi₂MoO₆@Bi₂MoO_{6-x} homojunction films for the enhanced visible-light-driven photocatalytic degradation of antibiotics, *Appl. Catal. B Environ.* 317 (2022) 121703, <https://doi.org/10.1016/j.apcatb.2022.121703>.
- [31] C. Munien, S. Rathilal, E.K. Tetteh, Challenges and prospects of TiO₂-based photocatalysis for wastewater treatment: keyword analysis, *Catalysts* 15 (2025) 801, <https://doi.org/10.3390/catal15090801>.
- [32] J. Arun, S. Nachiappan, G. Rangarajan, R.P. Alagappan, K.P. Gopinath, E. Lichtfouse, Synthesis and application of titanium dioxide photocatalysis for energy, decontamination and viral disinfection: a review, *Environ. Chem. Lett.* 21 (2023) 339–362, <https://doi.org/10.1007/s10311-022-01503-z>.
- [33] P. Vilarinho, J. Rigual-Miret, G. Farid, S. Chaitoglou, R. Amade, E. Gómez, A. Serrà, Temperature-tuned electrocatalytic valorization of levulinic acid to γ -valerolactone or 4-hydroxyvaleric acid over CuNi(Ru)/Graphene nanowalls, *ChemSusChem* 19 (2026) e205202403, <https://doi.org/10.1002/cssc.202502403>.
- [34] A. Lys, V. Myndrul, M. Pavlenko, B. Anastaziak, P. Holec, K. Vodešálková, E. Coy, M. Bechelany, I. Iatsunskyi, Electrospun polyimide nanofibers modified with metal oxide nanowires and MXene for photocatalytic water purification, *Nanomaterials* 15 (2025) 1371, <https://doi.org/10.3390/nano15171371>.
- [35] M. Ortiz, M. Gómez, A. Serrà, Recyclable biomimetic sunflower pollen-based photocatalyst for enhanced degradation of pharmaceuticals, *Small* 20 (2024) 2405204, <https://doi.org/10.1002/sml.202405204>.
- [36] E. Borràs, M. Aliaguilla, N. Bossa, S. Martínez-Crespiera, L. Huidobro, R. Schweiss, A. Schwenke, P. Bosch-Jimenez, Nanomaterials-based air-cathodes use in microbial desalination cells for drinking water production: Synthesis, performance and release assessment, *J. Environ. Chem. Eng.* 9 (2021) 105779, <https://doi.org/10.1016/j.jece.2021.105779>.
- [37] M. Abid, S. Sayegh, I. Iatsunskyi, E. Coy, G. Lesage, A. Ramanavicius, A. Ben Haj Amara, M. Bechelany, Design of halloysite-based nanocomposites by electrospinning for water treatment, *Colloids Surf. A Physicochem. Eng. Asp.* 651 (2022) 129696, <https://doi.org/10.1016/j.colsurfa.2022.129696>.
- [38] P. Qiu, R. Jin, Y. Son, A. Ju, W. Jiang, L. Wang, W. Luo, Mesoporous nanofibers from extended electrospinning technique, *Adv. Fiber Mater.* 6 (2024) 658–685, <https://doi.org/10.1007/s42765-024-00379-8>.
- [39] H. Zheng, H. Lu, S. Li, J. Niu, Y.K. Leong, W. Zhang, D.-J. Lee, J.-S. Chang, Recent advances in electrospinning-nanofiber materials used in advanced oxidation processes for pollutant degradation, *Environ. Pollut.* 344 (2024) 123223, <https://doi.org/10.1016/j.envpol.2023.123223>.
- [40] T.M. Howayek, M. Abid, H. Maslouh, R. Viter, D. Bezzerga, J. Hong, A.A. Nada, M. Cretin, I. Iatsunskyi, E. Coy, L. Assaud, D. Cornu, R. Habchi, M. Bechelany, TiO₂/SnO₂ photocatalysts by electrospinning and atomic layer deposition for pharmaceutical contaminant removal, *Journal Science Advanced Materials Devices* 10 (2025) 100945, <https://doi.org/10.1016/j.jsamd.2025.100945>.
- [41] S. Rajasri, S. Kalikeri, S. Balachandran, K. Gowthami, G. Thirunarayanan, M. Swaminathan, I. Muthuvel, Enhanced photodegradation of 2,4-dinitrophenol by n-p type TiO₂/BiOI nanocomposite, *J. Indian. Chem. Soc.* 99 (2022) 100337, <https://doi.org/10.1016/j.jics.2021.100337>.
- [42] B. Krishnakumar, R. Hariharan, V. Pandiyan, A. Aguiar, A.J.F.N. Sobral, Gelatin-assisted g-TiO₂/BiOI heterostructure nanocomposites for azo dye degradation under visible light, *J. Environ. Chem. Eng.* 6 (2018) 4282–4288, <https://doi.org/10.1016/j.jece.2018.06.035>.
- [43] V. Soni, M. Malhotra, A. Singh, A.A.P. Khan, S. Kaya, K. Katin, Q. Van Le, V.-H. Nguyen, T. Ahamad, P. Singh, P. Raizada, Unveiling cutting-edge developments in defective BiOI nanomaterials: Precise manipulation and improved functionalities towards bolstered photocatalysis, *Adv. Colloid Interface Sci.* 340 (2025) 103467, <https://doi.org/10.1016/j.cis.2025.103467>.
- [44] M. Tabassum, Aima-tul-aysha, B. Yang, X. Jia, M.N. Zafar, Progress on synthesis, characterization and photocatalytic applications of bismuth oxyhalide based nanomaterials in cleaner environment and energy - A review, *J. Clean. Prod.* 494 (2025) 144868, <https://doi.org/10.1016/j.jclepro.2025.144868>.
- [45] Y. Sun, C. Zeng, X. Zhang, Z. Zhang, B. Yang, S. Guo, Tendencies of alloyed engineering in BIOX-based photocatalysts: a state-of-the-art review, *Rare Met.* 43 (2024) 1488–1512, <https://doi.org/10.1007/s12598-023-02569-6>.
- [46] A.N. Arias-Sanchez, K. Flores, H. Fu, T. Betoni, P. Westerhoff, S. Garcia-Segura, Perspectives of electrochemical and photocatalytic technologies for the water-energy nexus potential of water splitting of brines, *Energy Clim. Change* 6 (2025) 100176, <https://doi.org/10.1016/j.egycc.2025.100176>.
- [47] J. Wei, F. Li, L. Zhou, D. Han, J. Gong, Strategies for enhancing peroxymonosulfate activation by heterogeneous metal-based catalysis: A review, *Chin. J. Chem. Eng.* 50 (2022) 12–28, <https://doi.org/10.1016/j.cjche.2022.07.032>.
- [48] D. Bertagna Silva, A.C. Marques, TiO₂-based photocatalytic degradation of microplastics in water: Current status, challenges and future perspectives, *J. Water Process. Eng.* 72 (2025) 107465, <https://doi.org/10.1016/j.jwpe.2025.107465>.
- [49] D. Li, K. Xu, C. Zhang, Improvement of photocatalytic performance by building multiple heterojunction structures of anatase–Rutile/BiOI composite fibers, *Nanomaterials* 12 (2022) 3906, <https://doi.org/10.3390/nano12213906>.
- [50] M. Abid, T.M. Howayek, O. Mazur, R. Viter, M.F. Bekheet, A.A. Nada, D. Bezzerga, J. Hong, P. Miele, I. Iatsunskyi, E. Coy, G. Lesage, R. Habchi, D. Cornu, M. Bechelany, Innovative electrospinning approach to fabricate TiO₂/NiO nanofibers for effective acetaminophen degradation, *Colloids Surf. A Physicochem. Eng. Asp.* 709 (2025) 136077, <https://doi.org/10.1016/j.colsurfa.2024.136077>.
- [51] M. Abid, A. Ben Haj Amara, M. Bechelany, Halloysite-TiO₂ Nanocomposites for Water Treatment: A Review, *Nanomaterials* 13 (2023) 1578, <https://doi.org/10.3390/nano13091578>.
- [52] Y. Liu, H. Wang, H. Qi, F. Qiao, S. Zhuang, Recent comprehensive review on synthesis, modification, applications, and advanced characterization of TiO₂ mesocrystals-based composite materials, *Catal. Rev.* (2024) 1–42, <https://doi.org/10.1080/01614940.2024.2446475>.
- [53] J. Musial, D.T. Mlynarczyk, B.J. Stanisz, Photocatalytic degradation of sulfamethoxazole using TiO₂-based materials – Perspectives for the development of a sustainable water treatment technology, *Sci. Total. Environ.* 856 (2023) 159122, <https://doi.org/10.1016/j.scitotenv.2022.159122>.
- [54] Q. Teng, X. Zhou, B. Jin, J. Luo, X. Xu, H. Guan, W. Wang, F. Yang, Synthesis and enhanced photocatalytic activity of a BiOI/TiO₂ nanobelt array for methyl orange degradation under visible light irradiation, *RSC Adv.* 6 (2016) 36881–36887, <https://doi.org/10.1039/C6RA01707J>.
- [55] A.C. Mera, C.A. Rodríguez, M.F. Meléndez, H. Valdés, Synthesis and characterization of BiOI microspheres under standardized conditions, *J. Mater. Sci.* 52 (2017) 944–954, <https://doi.org/10.1007/s10853-016-0390-x>.
- [56] J. Yin, G. Huang, H. Xiao, N. Chen, C. An, T.-C. Chao, R. Feng, S. Read, Bioinspired and dual-functional nanocellulose aerogels for water desinfection and heavy metal removal, *Nano Today* 51 (2023) 101918, <https://doi.org/10.1016/j.nantod.2023.101918>.
- [57] Y. Huang, Y. Jiang, Y. Wang, W. Zhao, Impact and penetration performance analysis of biomimetic 3D-printed hemispherical thin-shell composites inspired by silkworm cocoon, *Polym. Compos.* (2026) 1–19, <https://doi.org/10.1002/pc.70865>.
- [58] T.M. Howayek, M. Abid, H. Maslouh, R. Viter, I. Iatsunskyi, E. Coy, L. Assaud, D. Cornu, R. Habchi, M. Bechelany, Silver-doped TiO₂/SnO₂ for enhanced visible-light-driven photocatalytic degradation of acetaminophen, *Mater. Today Commun.* 50 (2026) 114635, <https://doi.org/10.1016/j.mtcomm.2026.114635>.
- [59] M. Rohan Khizer, Z. Saddique, M. Imran, A. Javid, S. Latif, D. Mantzavinos, M. Momotko, G. Boczkaj, Polymer and graphitic carbon nitride based nanohybrids for the photocatalytic degradation of pharmaceuticals in wastewater treatment – A review, *Sep. Purif. Technol.* 350 (2024) 127768, <https://doi.org/10.1016/j.seppur.2024.127768>.
- [60] Z. Jiao, S. Zhang, C. Zhao, X. Li, Z. Wang, J. Zhao, H. Ding, B. Li, S. Niu, Z. Han, Broadband and omnidirectional antireflective film with bioinspired nanocane-grid hybrid structures for enhanced solar energy harvesting, *Nanoscale* 18 (2026) 481–495, <https://doi.org/10.1039/D5NR03946K>.
- [61] R.V. Nair, V.S. Gummaluri, M.V. Matham, V. C, A review on optical bandgap engineering in TiO₂ nanostructures via doping and intrinsic vacancy modulation towards visible light applications, *J. Phys. D Appl. Phys.* 55 (2022) 313003, <https://doi.org/10.1088/1361-6463/ac6135>.
- [62] M. Răpă, B. Alhalaili, F.A. Dincă, A.M. Predescu, E. Matei, R. Vidu, Hybrid Electrospun conductive nanofibers for emerging organic contaminants' degradation in visible light photocatalysis: a review, *Int. J. Mol. Sci.* 26 (2025) 9055, <https://doi.org/10.3390/ijms26189055>.
- [63] A.M. Nasir, N. Awang, J. Jaafar, A.F. Ismail, M.H.D. Othman, M. A. Rahman, F. Aziz, M.A. Mat Yajid, Recent progress on fabrication and application of electrospun nanofibrous photocatalytic membranes for wastewater treatment: A review, *J. Water Process. Eng.* 40 (2021) 101878, <https://doi.org/10.1016/j.jwpe.2020.101878>.
- [64] R.B.P. Marcelino, C.C. Amorim, Towards visible-light photocatalysis for environmental applications: band-gap engineering versus photons absorption—a review, *Environ. Sci. Pollut. Res.* 26 (2019) 4155–4170, <https://doi.org/10.1007/s11356-018-3117-5>.
- [65] K.C. Hui, H. Suhaimi, N.S. Sambudi, Electrospun-based TiO₂ nanofibers for organic pollutant photodegradation: a comprehensive review, *Rev. Chem. Eng.* 38 (2022) 641–668, <https://doi.org/10.1515/revce-2020-0022>.
- [66] A. Esmaili-Baghi-Karimabad, D. Ghanbari, M. Salavati-Niasari, L. Nejati-Moghadam, S. Gholamrezaei, Photo-catalyst thin dioxide: synthesis and characterization different morphologies of SnO₂ nanostructures and nanocomposites, *J. Mater. Science Mater. Electron.* 26 (2015) 6970–6978, <https://doi.org/10.1007/s10854-015-3316-5>.
- [67] M. Khairy, M.M. Mohamed, K.A. Soliman, E.M. Masoud, M. Sameeh, Boosting ciprofloxacin and indigo carmine dye photodegradation using S-scheme plate-like BiOI/sulfated TiO₂ heterojunctions: An understanding of the performance, the degradation route, and DFT computation, *J. Environ. Manag.* 370 (2024) 123032, <https://doi.org/10.1016/j.jenvman.2024.123032>.
- [68] R.M. Matir, A.A. Abuelwafa, S. Kato, N. Kishi, T. Soga, A comparative study on optical properties of BiOI, Bi₂O₃I₃ and Bi₂O₃I materials, *Opt. Mater.* 111 (2021) 110677, <https://doi.org/10.1016/j.optmat.2020.110677>.
- [69] M. Wang, K. Wang, Y. Yang, Y. Liu, D.G. Yu, Electrospun environment remediation nanofibers using unspinnable liquids as the sheath fluids: A review, *Polymers* 12 (2020) 103, <https://doi.org/10.3390/POLY12010103>.

- [70] S.-Y. Murakami, H. Kominami, Y. Kera, S. Ikeda, H. Noguchi, K. Uosaki, B. Ohtani, Evaluation of electron-hole recombination properties of titanium(IV) oxide particles with high photocatalytic activity, *Res. Chem. Intermed.* 33 (2007) 285–296, <https://doi.org/10.1163/156856707779238612>.
- [71] Y. Quan, M.H.N. YiO, Y. Li, R.J. Myers, A. Kafizas, Influence of Bi co-catalyst particle size on the photocatalytic activity of BiOI microflowers in Bi/BiOI junctions – A mechanistic study of charge carrier behaviour, *J. Photochem. Photobiol. A Chem.* 443 (2023) 114889, <https://doi.org/10.1016/j.jphotochem.2023.114889>.
- [72] S. Yueyu, The synergistic degradation of pollutants in water by photocatalysis and PMS activation, *Water Environ. Res.* 95 (2023) e10927, <https://doi.org/10.1002/wer.10927>.
- [73] Y. Ding, X. Wang, L. Fu, X. Peng, C. Pan, Q. Mao, C. Wang, J. Yan, Nonradicals induced degradation of organic pollutants by peroxydisulfate (PDS) and peroxymonosulfate (PMS): Recent advances and perspective, *Sci. Total. Environ.* 765 (2021) 142794, <https://doi.org/10.1016/j.scitotenv.2020.142794>.
- [74] J. Wang, D. Zhi, H. Zhou, X. He, D. Zhang, Evaluating tetracycline degradation pathway and intermediate toxicity during the electrochemical oxidation over a Ti/Ti₄O₇ anode, *Water Res.* 137 (2018) 324–334, <https://doi.org/10.1016/j.watres.2018.03.030>.
- [75] N. Li, J. Ye, H. Dai, P. Shao, L. Liang, L. Kong, B. Yan, G. Chen, X. Duan, A critical review on correlating active sites, oxidative species and degradation routes with persulfate-based antibiotics oxidation, *Water Res.* 235 (2023) 119926, <https://doi.org/10.1016/j.watres.2023.119926>.
- [76] P.V. Nidheesh, K. Kaur, R.G. Anukrishna, K.P. Prathish, From scavenger to catalyst: the emerging role of chloride in peroxymonosulfate-based advanced oxidation processes, *Environmental Science Water Research & Technology* 11 (2025) 2480–2498, <https://doi.org/10.1039/D5EW00674K>.
- [77] X. Wang, Y. Chen, ZnIn₂S₄/CoFe₂O₄ p-n junction-decorated biochar as magnetic recyclable nanocomposite for efficient photocatalytic degradation of ciprofloxacin under simulated sunlight, *Sep. Purif. Technol.* 303 (2022) 122156, <https://doi.org/10.1016/j.seppur.2022.122156>.
- [78] D. Kong, H. Fan, D. Yin, D. Zhang, X. Pu, S. Yao, C. Su, AgFeO₂ nanoparticle/ZnIn₂S₄ microsphere p–n heterojunctions with hierarchical nanostructures for efficient visible-light-driven H₂ evolution, *ACS Sustain. Chem. Eng.* 9 (2021) 2673–2683, <https://doi.org/10.1021/acssuschemeng.0c07638>.
- [79] X. Jiang, D. Fan, X. Yao, Z. Dong, X. Li, S. Ma, J. Liu, D. Zhang, H. Li, X. Pu, P. Cai, Highly efficient flower-like ZnIn₂S₄/CoFe₂O₄ photocatalyst with p-n type heterojunction for enhanced hydrogen evolution under visible light irradiation, *J. Colloid Interface Sci.* 641 (2023) 26–35, <https://doi.org/10.1016/j.jcis.2023.03.055>.
- [80] Preethi, S.P. Shanmugavel, G. Kumar, Y.K. N, G. M, R.B. J, Recent progress in mineralization of emerging contaminants by advanced oxidation process: A review, *Environ. Pollut.* 341 (2024) 122842, <https://doi.org/10.1016/j.envpol.2023.122842>.
- [81] V. Thakur, S. Singh, P. Kumar, S. Rawat, V. Chandra Srivastava, S.L. Lo, U. Lavrenčić Stangar, Photocatalytic behaviors of bismuth-based mixed oxides: Types, fabrication techniques and mineralization mechanism of antibiotics, *Chem. Eng. J.* 475 (2023) 146100, <https://doi.org/10.1016/j.cej.2023.146100>.
- [82] Z. Kása, E. Bárdos, E. Kása, T. Gyulavári, L. Baia, Z. Pap, K. Hernadi, Myth or reality? A disquisition concerning the photostability of bismuth-based photocatalysts, *J. Environ. Chem. Eng.* 10 (2022) 107624, <https://doi.org/10.1016/j.jece.2022.107624>.
- [83] H. Mohan, S.S. Rajput, E.B. Jadhav, M.S. Sankhla, S.S. Sonone, S. Jadhav, R. Kumar, Ecotoxicity, occurrence, and removal of pharmaceuticals and illicit drugs from aquatic systems, *Biointerface Res. Appl. Chem.* 11 (2021) 12530–12546, <https://doi.org/10.33263/BRIAC115.1253012546>.
- [84] C. Fang, J. Yan, Y. Wang, N. Zhang, X. Liu, Facile synthesis of N-doped carbon nanorods for antibiotics degradation via PMS activation: Mechanism insight and biotoxicity assessment, *Sep. Purif. Technol.* 340 (2024) 126849, <https://doi.org/10.1016/j.seppur.2024.126849>.
- [85] W. Hamd, E.A. Daher, T.S. Tofa, J. Dutta, Recent advances in photocatalytic removal of microplastics: mechanisms, kinetic degradation, and reactor design, *Front. Mar. Sci.* 9 (2022) 885614, <https://doi.org/10.3389/fmars.2022.885614>.
- [86] A.A. Koelmans, P.E. Redondo-Hasselerharm, N.H.M. Nor, V.N. De Ruijter, S. M. Mintenig, M. Kooi, Risk assessment of microplastic particles, *Nat. Rev. Mater.* 7 (2022) 138–152, <https://doi.org/10.1038/s41578-021-00411-y>.
- [87] M.C. Ariza-Tarazona, C. Siligardi, H.A. Carreón-López, J.E. Valdéz-Cerda, P. Pozzi, G. Kaushik, J.F. Villarreal-Chiu, E.I. Cedillo-González, Low environmental impact remediation of microplastics: Visible-light photocatalytic degradation of PET microplastics using bio-inspired C,N-TiO₂/SiO₂ photocatalysts, *Mar. Pollut. Bull.* 193 (2023) 115206, <https://doi.org/10.1016/j.marpolbul.2023.115206>.
- [88] X. Liu, Z. Yang, H. Liu, Y. Li, G. Zhang, Efficient photocatalytic degradation of microplastics by constructing a novel Z-scheme Fe-doped BiO_{2-x}/BiOI heterojunction with full-spectrum response: Mechanistic insights and theory calculations, *J. Hazard. Mater.* 480 (2024) 136080, <https://doi.org/10.1016/j.jhazmat.2024.136080>.