Practical Application of COF Materials in Catalyzing the Degradation of Antibiotic Residues in Natural Environments

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Abstract. This study develops a recoverable photosensitive covalent organic framework (COF) thin-film catalyst for visible-light degradation of tetracycline (TC), ciprofloxacin (CIP), and sulfamethazine (SMR). Imine-linked COF films were prepared by liquid-liquid interfacial synthesis and coupled with TiO_2 to form an S-scheme heterojunction intended to strengthen light harvesting, charge separation, and reactive oxygen species generation. Under simulated visible light ($\lambda > 420$ nm), the reported end-point degradation efficiencies were 94.8% for TC, 91.2% for CIP, and 88.5% for SMR. The relative performance indicates that molecular structure and catalyst-pollutant affinity affect removal, while the film configuration improves catalyst recovery compared with dispersed powders. These results support COF/TiO_2 films as a promising platform for antibiotic treatment, although mineralization, intermediate toxicity, cycling stability, and performance in real wastewater require further verification.

Keywords: Covalent organic frameworks (COFs); photocatalysis; antibiotic degradation; S-scheme heterojunction; photosensitive groups; interfacial synthesis; water pollution treatment.

1. Introduction

Antibiotics have played an irreplaceable role in modern medicine since the discovery of penicillin in 1928 [1]. They have greatly reduced deaths caused by bacterial infections and have been widely used in clinical treatment, animal husbandry, and related fields. However, large-scale use, misuse, and incomplete wastewater treatment have also caused antibiotics to enter natural water bodies. Even at relatively low concentrations, antibiotic residues may affect aquatic organisms, disturb microbial communities, and increase selective pressure for antibiotic-resistant bacteria [2-4]. Therefore, the removal of antibiotic residues from wastewater is not only an environmental issue but also a public-health concern.

Natural enzymes show high catalytic efficiency under mild conditions, but their poor operational stability, complex preparation, and strict storage requirements limit continuous water-treatment use. Conventional inorganic catalysts can be more robust, yet catalyst recovery, secondary particle release, and insufficient visible-light utilization remain practical concerns. These limitations have encouraged the development of artificial enzyme mimics that combine catalytic activity with better stability and manufacturability [5, 6].

Nanozymes are an important type of artificial enzyme mimic. Compared with many biological catalysts, they are easier to prepare, more stable, and more suitable for large-scale use [5,6]. Among various nanozyme materials, covalent organic frameworks (COFs) are especially attractive. COFs are porous crystalline materials constructed from organic monomers through covalent bonds [7]. Their ordered framework, adjustable pore structure, and abundant functional sites allow researchers to design catalytic centers according to specific reaction needs [8]. In the degradation of antibiotic residues, COFs can adsorb pollutant molecules, promote photocatalytic reactions, and provide a platform for multi-component catalytic systems [8,12].

Despite rapid progress in COF photocatalysis, many studies emphasize material synthesis or single-pollutant performance, while recoverability and cross-antibiotic comparison receive less attention. This study therefore focuses on a photosensitive COF thin film prepared by interfacial synthesis [9], strengthened through functional-group design and an S-scheme COF/TiO_2 heterojunction [10,11], and evaluated against TC, CIP, and SMR. The central question is not only whether high removal can be achieved, but whether the material form and reaction design provide a credible route toward reusable water-treatment catalysts.

2. Catalyst Design and Synthesis

The COF catalyst was designed as a photosensitive thin film. This form was selected as an engineering choice, not merely a synthetic preference: a self-supporting film can be removed directly from treated water, whereas a powder normally requires sedimentation, centrifugation, or membrane separation. Interfacial synthesis can form continuous COF films under mild conditions because monomer diffusion and polymerization are confined near the boundary of two immiscible phases [9]. The same diffusion control may, however, create thickness gradients or fragile regions if the interface is disturbed, so reproducible scale-up will depend on tight control of monomer concentration, phase contact area, and reaction time.

In the present synthesis route, aldehyde and amine monomers were used to form imine-linked COF structures [8,9]. Ultrapure water containing acetic acid served as the aqueous phase, while dichloromethane was used as the organic phase to dissolve the aldehyde monomer. Acetic acid promoted the imine condensation reaction, and the stable interface restricted the reaction to a thin region between the two liquids. Because the reaction was reversible, structural defects could be partially corrected during crystal growth, improving the order and stability of the final COF material.

The system was kept still after the two phases were combined so that the interface remained stable. Small crystalline domains first appeared at the interface and then connected into a continuous film. After the reaction was completed, the COF film was collected, washed to remove residual monomers and solvents, and dried for later catalytic experiments. This procedure simplified the preparation process and produced a regular two-dimensional film structure with favorable exposure of active sites.

Photosensitive units such as porphyrin, pyrene, triazine, benzothiadiazole, and triphenylamine can broaden COF light absorption [8]. In the present design, coupling the COF with TiO_2 is intended to overcome two separate limitations: restricted visible-light response and rapid recombination of photogenerated carriers. The S-scheme interpretation is plausible because it retains carriers with stronger oxidation and reduction potentials [10,11]. Nevertheless, improved degradation alone does not prove an S-scheme pathway; band-position measurements, radical trapping, and spectroscopic evidence are needed to distinguish it from ordinary charge transfer. Figure 1 summarizes the proposed, rather than conclusively proven, catalytic mechanism.

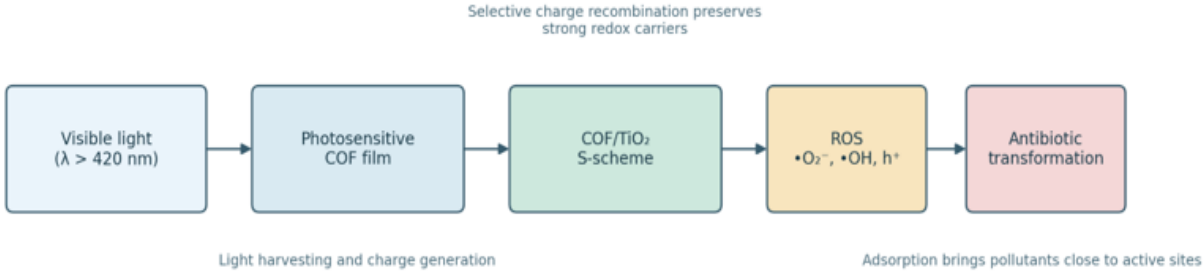


Figure 1. Proposed visible-light degradation pathway in the COF/TiO_2 thin-film system.

3. Experimental Evaluation

The degradation experiments selected tetracycline (TC), ciprofloxacin (CIP), and sulfamethazine (SMR) as representative antibiotic pollutants. These antibiotics have been widely used in medical or agricultural contexts and can enter natural environments through wastewater discharge [2,12,13]. TC represents a broad-spectrum antibiotic with frequent environmental detection; CIP is a commonly used fluoroquinolone with strong antibacterial activity; and SMR is difficult to biodegrade and has notable persistence in water environments [12,13].

Stock solutions of the three antibiotics were prepared with ultrapure water and diluted before use. The experimental concentration range was 20-100 mg/L for TC, 10-25 mg/L for CIP, and a concentration for SMR determined by preliminary tests. The photocatalytic degradation tests were carried out in a quartz reactor under simulated visible-light irradiation provided by a 300 W xenon

lamp equipped with a UV cutoff filter (λ > 420 nm). The pH was adjusted with dilute HCl or NaOH when necessary, and the system was protected from external stray light.

In each experiment, 100 mL of antibiotic solution was placed in the reactor, and one COF film was vertically immersed in the solution. Before irradiation, the system was stirred in the dark for 30 minutes to establish adsorption-desorption equilibrium. Samples were then collected at selected time points during illumination, immediately filtered through a hydrophilic membrane, and stored in amber vials at 4 °C before analysis.

The concentrations of TC, CIP, and SMR were determined by high-performance liquid chromatography using a reversed-phase C18 column. The mobile phase and detection wavelength were adjusted according to the target antibiotic: TC was detected at 355 nm, CIP at 278 nm, and SMR at 264 nm. Each degradation experiment was repeated three times. Direct photolysis tests without catalyst and dark adsorption controls were also conducted to distinguish photocatalytic degradation from simple adsorption or light-induced self-decomposition.

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The degradation efficiency was calculated according to the equation: Degradation efficiency (%) = (C0 - Ct) / C0 x 100%, where C0 is the concentration after dark adsorption equilibrium and Ct is the concentration after irradiation for time t. To identify the major active species, isopropanol, p-benzoquinone, and EDTA-2Na were added separately as scavengers for hydroxyl radicals, superoxide radicals, and photogenerated holes, which are commonly discussed in photocatalytic antibiotic-degradation studies [12,13]. Total organic carbon measurements and, when necessary, LC-MS analysis were used to evaluate mineralization and possible degradation intermediates. The experimental concentration ranges, HPLC detection wavelengths, control conditions, and replication are summarized in Table 1.

Table 1. Experimental design and analytical controls used in this study.

Item	TC	CIP	SMR	Purpose / author assessment
Initial range	20–100 mg/L	10–25 mg/L	Set by preliminary tests	The unequal ranges reflect compound-specific detectability and response; direct comparison should therefore rely on normalized removal, not raw concentration loss.
HPLC wavelength	355 nm	278 nm	264 nm	Compound-specific detection reduces spectral mismatch during quantification.
Controls	No catalyst; dark adsorption	No catalyst; dark adsorption	No catalyst; dark adsorption	These controls separate photocatalysis from adsorption and direct photolysis.
Replication	n = 3	n = 3	n = 3	Replicates support repeatability, but means should be reported with standard deviations in future work.

4. Results and Discussion

As summarized in Table 2, the prepared COF thin film showed visible-light activity toward all three antibiotics. TC reached 94.8% degradation after 90 min, CIP reached 91.2%, and SMR reached 88.5% after 150 min. The 6.3-percentage-point spread between TC and SMR is modest in absolute terms, but the longer SMR treatment indicates that end-point percentage alone can overstate comparability. On the evidence available, the most defensible conclusion is that the catalyst has broad substrate applicability, not that the three compounds react at the same rate.

Table 2. Comparative degradation of performance and interpretation.

Antibiotic	End-point degradation	Reported irradiation time	Difference from TC	Author interpretation
TC	94.8%	90 min	Reference	Highest observed removal; favorable adsorption and/or oxidative susceptibility may contribute.
CIP	91.2%	Not separately stated	−3.6 percentage points	High removal, but a kinetic comparison requires the corresponding sampling time and rate constant.
SMR	88.5%	150 min	−6.3 percentage points	Lower removal over a longer period suggests greater persistence under the tested conditions.

The observed activity is consistent with a three-stage process: pollutant enrichment at the aromatic porous surface, photoinduced charge generation, and reactive-species attack. π–π interactions, hydrogen bonding, and electrostatic attraction can raise the local antibiotic concentration near active sites [8]. The COF/TiO_2 interface can then extend light use and suppress unproductive carrier recombination. In the authors' judgment, adsorption and photocatalysis should be treated as coupled rather than competing mechanisms: adsorption is beneficial only when it delivers molecules to reactive sites without blocking light or saturating pores. This balance may partly explain the different responses of TC, CIP, and SMR.

The material reportedly retained favorable physicochemical properties and catalytic performance from pH 1 to 13. If confirmed by quantitative activity and structural data at each pH, this would be unusually valuable for variable wastewater. At present, however, the broad claim should be interpreted cautiously because retained appearance or crystallinity does not necessarily mean unchanged catalytic kinetics. A stronger demonstration would combine degradation-rate constants, PXRD/FTIR data before and after reaction, and leaching measurements.

The film form offers a clear operational advantage over powders by reducing catalyst loss and simplifying recovery. Yet recoverability is not equivalent to reusability. Repeated-cycle efficiency, mechanical integrity, active-site fouling, and Ti or organic-component leaching must be quantified before practical deployment. Likewise, disappearance of the parent antibiotic does not demonstrate detoxification: total organic carbon, LC–MS intermediates, and bioassays are needed to determine whether treatment achieves mineralization or merely converts one bioactive molecule into others. These considerations define the main gap between the promising laboratory result and an environmentally credible treatment process.

5. Conclusions and Prospects

This study shows that a photosensitive COF/TiO_2 thin film can combine visible-light photocatalysis with a recoverable catalyst format. Interfacial synthesis produced an imine-linked film, while photosensitive units and the proposed S-scheme interface were used to improve light utilization and preserve strong redox carriers.

Under the tested conditions, the reported end-point degradation efficiencies were 94.8% for TC, 91.2% for CIP, and 88.5% for SMR. The results support broad antibiotic-removal capability, but they also show why end-point percentages must be interpreted together with reaction time and kinetic data. The film geometry is practically important because it can simplify catalyst recovery and reduce the risk of residual particles in treated water.

The immediate research priorities are to report complete kinetics with uncertainty, verify the proposed charge-transfer mechanism, quantify mineralization and intermediate toxicity, and test repeated use in real wastewater. Addressing these points will determine whether the material is only an effective laboratory photocatalyst or a robust treatment platform suitable for environmental application.

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