

Supplementary Materials

Experimental Section

Chemicals

Sodium hydroxide (granular, NaOH), ethylene glycol, anhydrous ethanol, isopropyl alcohol, and methanol were purchased from China National Pharmaceutical Group Chemical Reagent Co., Ltd. Titanium dioxide (TiO₂) was purchased from China Aladdin Reagent Co., Ltd. Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) was purchased from Sigma-Aldrich.

Material Characterization

The crystal structure of Bi₄Ti₃O₁₂ was determined by X-ray diffraction (XRD, Ultima IV) using a Cu K α radiation source with a scanning range of 10–80° and a scanning rate of 10°/min. The surface morphology of the samples was characterized by scanning electron microscopy (SEM, JSM 2100). The ultraviolet-visible diffuse reflectance spectra (UV-DRS) of the samples were measured using a Shimadzu UV-2550 spectrophotometer within the wavelength range of 200–800 nm. Surface defects in the samples were analyzed using an electron paramagnetic resonance (ESR) spectrometer (Brooke ESM). Photo/electrochemical measurements were performed on samples via a standard three-electrode system using an electrochemical workstation (CHI 760E), with platinum wire, Ag/AgCl, and the test sample serving as the auxiliary electrode, reference electrode, and working electrode, respectively. Photocurrent and electrochemical impedance spectroscopy measurements were conducted in Na₂SO₄ electrolyte (0.2 mol/L) and impedance buffer (K₄[Fe(CN)₆], 5 mmol/L), respectively. Finally, degradation intermediates of ciprofloxacin were detected using high-resolution mass spectrometry (HRMS, Agilent qTOF 6550).

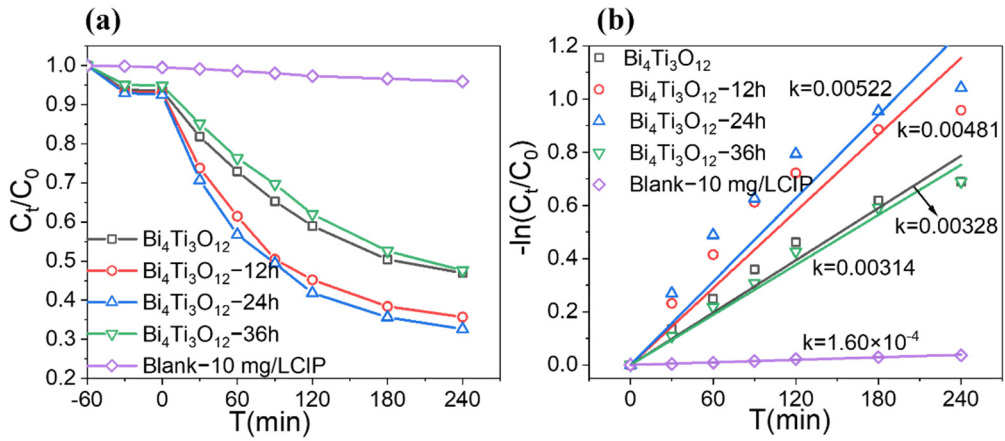


Figure S1. (a) Degradation curves and (b) kinetic curves of CIP with different catalysts.

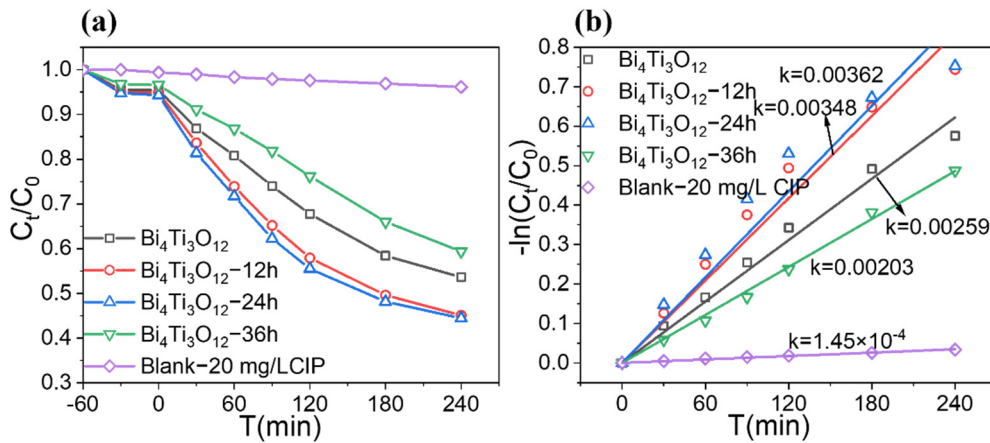


Figure S2. (a) Degradation curves and (b) kinetic curves of CIP with different catalysts.

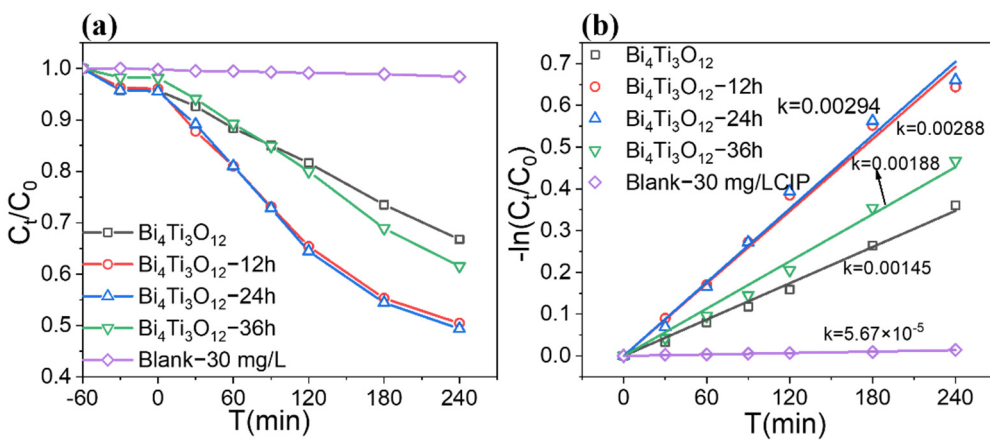


Figure S3. (a) Degradation curves and (b) kinetic curves of CIP with different catalysts.

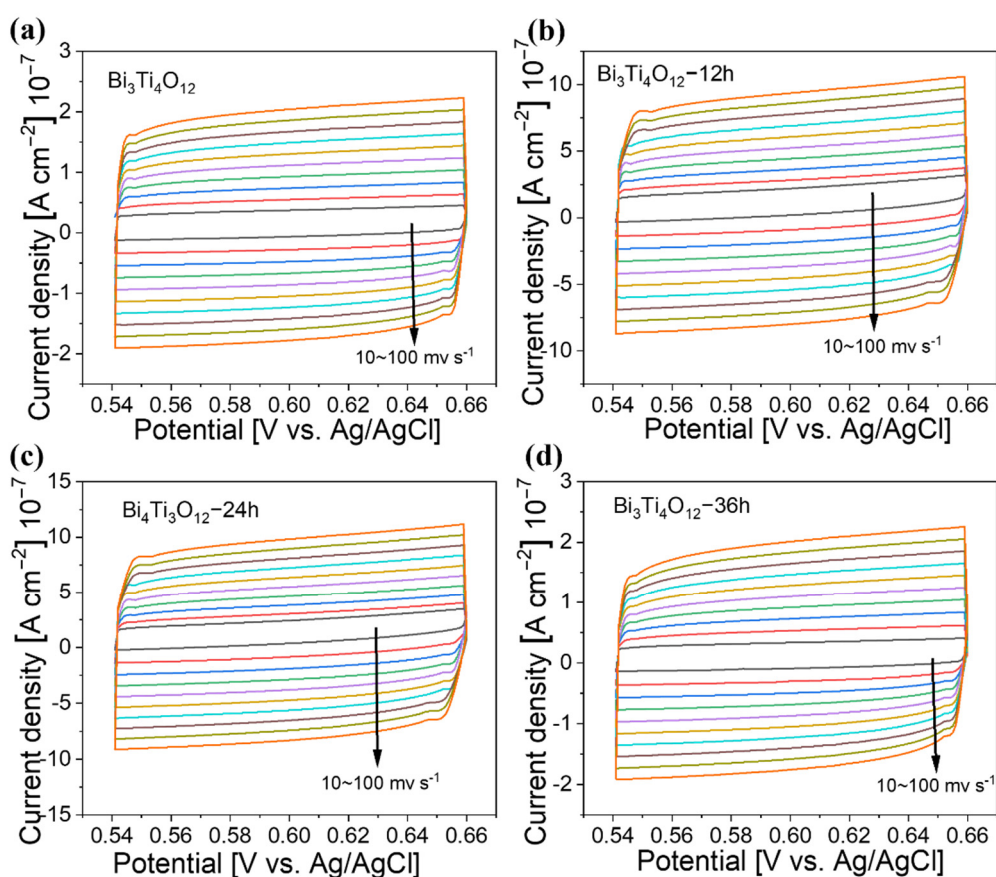


Figure S4. Cyclic voltammetric curve of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (a), $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -12h (b), $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -24h (c), and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -36h (d).

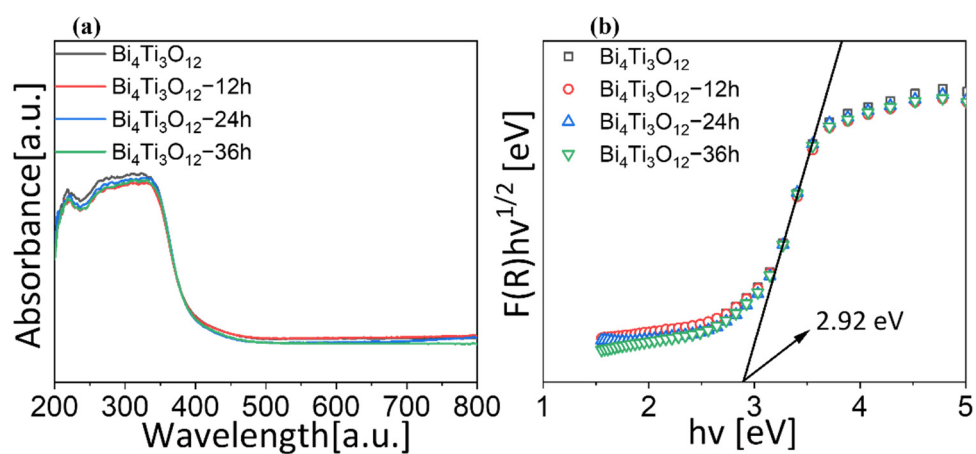


Figure S5. UV-DRS (a) and bandgap (b) of the sample $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -12h, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -24h, and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -36h.

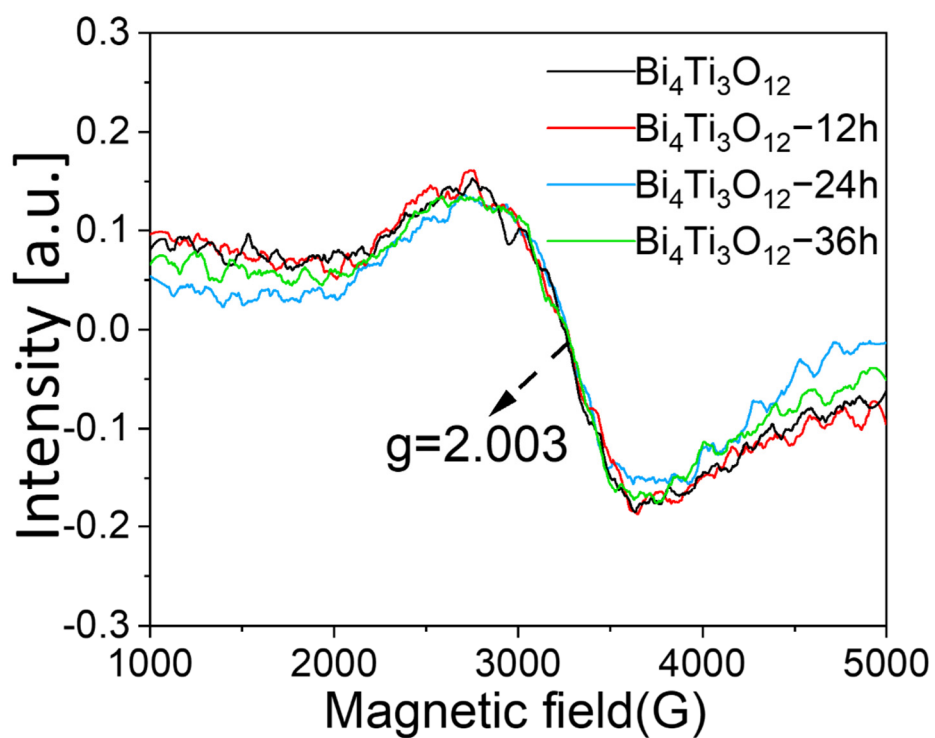


Figure S6. EPR of the sample $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -12h, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -24h, and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -36h.

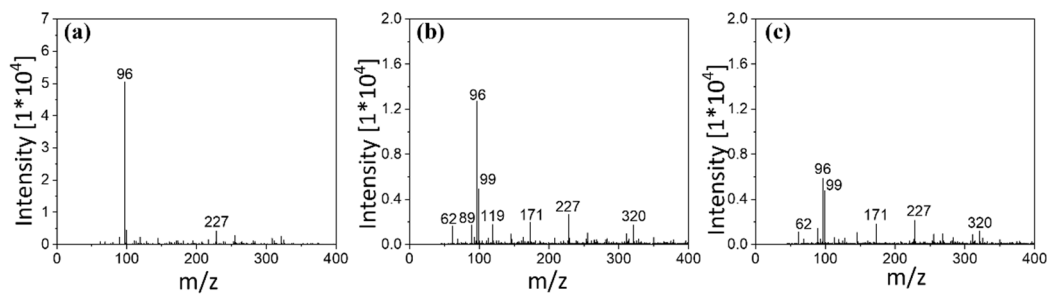


Figure S7. HRMS spectra at degradation times of (a) 30, (b) 120, and (c) 240 min.

Table S1. A comparative study on photocatalytic degradation of CIP with different photocatalysts.

| Photocatalyst | Light Source | CIP Concentration | Reaction Kinetics | Refs |
|---|---------------|-------------------|---------------------------|-----------|
| g-C ₃ N ₄ /BiOCl-2 | 300 W Xe lamp | 10 mg/L | 0.0015 min ⁻¹ | [1] |
| BiOBr | 300 W Xe lamp | 10 mg/L | 0.00244 min ⁻¹ | [2] |
| Fe ₂ O ₃ /TiO ₂ /diatomite-5 | 300 W Xe lamp | 5 mg/L | 0.00241 min ⁻¹ | [3] |
| BiOCl/Uio-66-NH ₂ | 300 W Xe lamp | 10 mg/L | 0.0018 min ⁻¹ | [4] |
| Bi ₄ Ti ₃ O ₁₂ -24h | 300 W Xe lamp | 40 mg/L | 0.00245 min ⁻¹ | This work |

Reference

- [1] Y. Lin, Y. Wang, C. Shi, D. Zhang, G. Liu, L. Chen, B. Yuan, A. Hou, D. Zou, X. Liu, Q. Zhang, Degradation of ciprofloxacin by a constitutive g-C₃N₄/BiOCl heterojunction under a persulfate system, *RSC Advances*, 13 (2023) 4361-4375.
- [2] X. Chen, X. Gao, L. Ai, H. Fan, Triton X-100-assisted synthesis of layered nanosheet-assembled flower-like BiOBr nanostructures with enhanced visible-light photocatalytic degradation of ciprofloxacin, *J. Nanopart. Res.*, 24 (2022) 103.
- [3] X. Zhang, J. Duan, Y. Tan, Y. Deng, C. Li, Z. Sun, Insight into peroxymonosulfate assisted photocatalysis over Fe₂O₃ modified TiO₂/diatomite composite for highly efficient removal of ciprofloxacin, *Sep. Purif. Technol.*, 293 (2022) 121123.
- [4] H. Luo, J. Wang, J. Chen, X. Li, Ag QDs modified BiOCl/Uio-66-NH₂ Z-scheme heterojunction for accelerated visible light-driven photocatalytic degradation of ciprofloxacin, *J. Environ. Chem. Eng.*, 12 (2024) 114299.