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Supporting Information

Covalent Organic Framework-Supported Fe-TiO_2 Nanoparticles as Ambient-Light-Active Photocatalysts

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1. Materials and general methods

All commercially available reagents and solvents were used as received without further purification, unless noted otherwise. 1, 3, 5-triformylphloroglucinol (Tp) was synthesized according to the literature procedure [1]. The FT-IR spectra of starting materials and as synthesized TpTa-COF were obtained from Agilent Technologies Cary 630 FT-IR. The powder wide angle X-ray diffraction pattern (PXRD) of TpTa-COF was recorded on an X`Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source (λ = 1.540598 Å), those of TiO_2, 5Fe-TiO_2 and 5Fe-TiO_2@COF were recorded on a DX-2700BH X-ray diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source (λ = 1.540598 Å). The Quantachrome Autosorb ASiQ automated gas sorption analyzer was used to measure N_2 adsorption isotherm. The morphologies of the COF and the NPs were observed by scanning electron microscope (FEI Nova NanoSEM 450) and transmission electron microscope (JEM2100). The EDS spectra were obtained by scanning electron microscope (Hitachi, S3400N). Photoluminescence spectra (PL) were obtained by a FL4500 fluorescence spectrophotometer (Shimadzu). UV-vis absorption spectra for MB degradation were obtained with an Agilent 8453 spectrophotometer, and those for TiO_2, 5Fe-TiO_2 and 5Fe-TiO_2@COF were obtained with a Metash UV-9000S spectrophotometer. The composition and chemical state of as-prepared NPs were characterized by X-ray photoelectron spectroscopy (XPS, PHI5000 Versaprobe-II) with Al X-ray radiation at a working power of 50 W. Ultraviolet Photoelectron Spectroscopy (XPS) was conducted on a Thermo ESCALAB 250Xi tester with the Al Ka as X-ray source. Nuclear magnetic resonance (NMR) spectra were obtained on the AVANCEIIIHD600 spectrometer.

2. Synthetic procedure

Synthesis of TpTa-COF: The procedure reported in the literature was followed [2]. To an ampoule (the outer diameter is 10 mm and the inner diameter is 8 mm) were added trialdehyde Tp (11 mg, 0.05 mmol), *p*-tertphenyl, 4’-4’’-diamine (Ta, 17 mg, 0.075 mmol), 6 M acetic acid (0.2 mL), dioxane (0.6 mL), and mesitylene (0.6 mL). The tube was flash frozen at 77 K in liquid nitrogen and evacuated to the internal pressure of ~90 mTorr. The tube was sealed under an open flame. The mixture was first warmed to room temperature and then the temperature was slowly raised to 120 °C over 2 h. The reaction was kept at this temperature for 3 days and cooled to room temperature over 12 h. The orange precipitate was collected by vacuum filtration, washed with a large amount of acetone and tetrahydrofuran, and dried under vacuum to yield COF.

3. The photocatalytic degradation of the samples with different loading amount of Fe-TiO_2 on COF

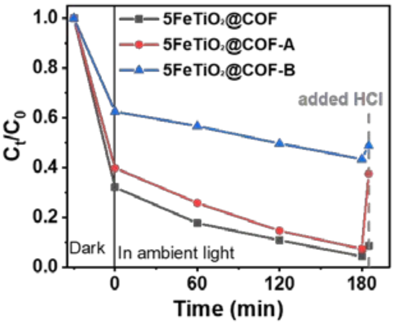


Fig. S1 The photocatalytic degradation performance of 5Fe-TiO_2@COF-A and 5Fe-TiO_2@COF-B, prepared from 5 mg TpTa-COF and 1.5 mL or 5.0 mL of Ti(O^{n}Bu)$_4$, respectively, following the same procedure for the preparation of 5Fe-TiO_2@COF. The degradation experiments were performed with 40 mg L^{-1} MB in the ambient light (3 h). After each reaction, two drops of conc. HCl was added to release the physically adsorbed MB. Clearly, 5Fe-TiO_2@COF has higher catalytic activity compared to 5Fe-TiO_2@COF-A and 5Fe-TiO_2@COF-B, indicating there is optimal dosage of Ti species for the preparation of 5Fe-TiO_2@COF catalysts.

4. XPS spectra and EDS spectra

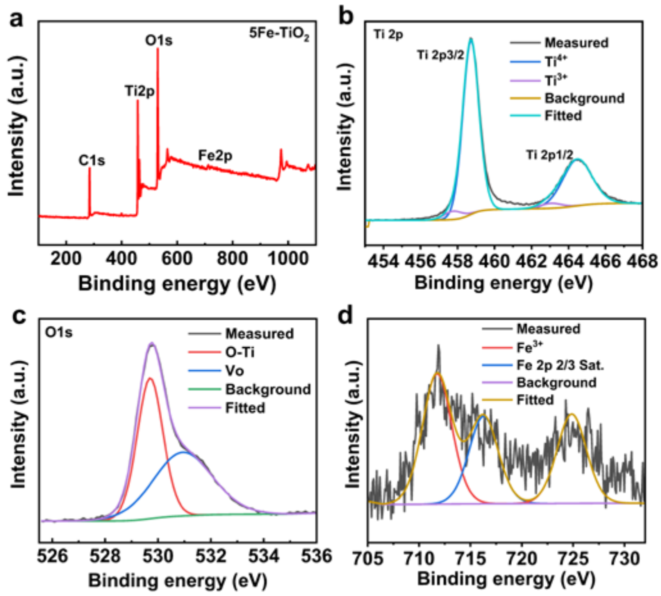


Fig. S2 The XPS spectra of 5Fe-TiO_2 (a), high resolution XPS spectra of each element in 5Fe-TiO_2 (b-d).

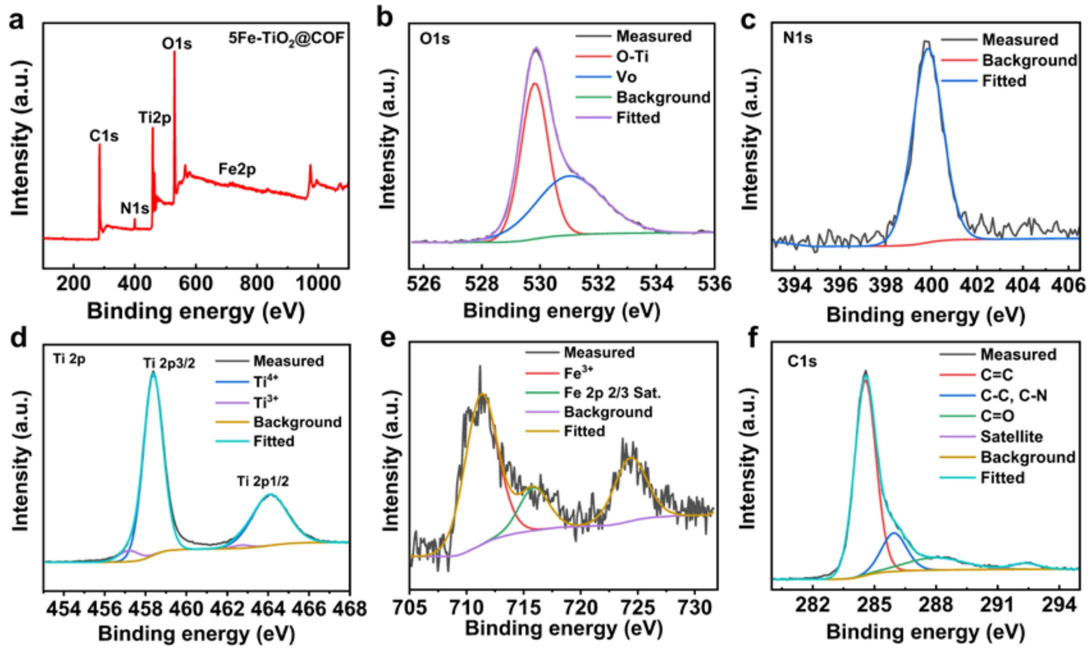


Fig. S3 The XPS spectra of 5Fe-TiO$_2$@COF (a), high resolution XPS spectra of each element in 5Fe-TiO$_2$@COF (b-f).

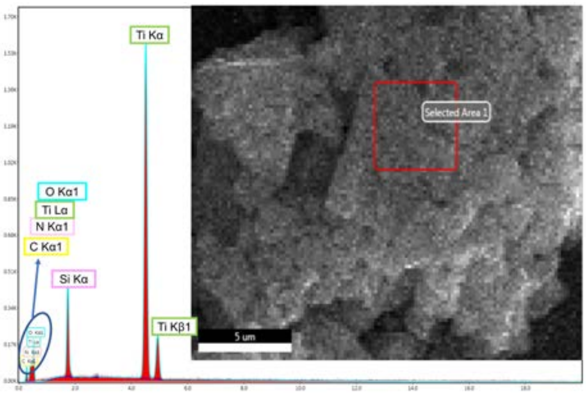


Fig. S4 The EDS spectrum of TiO$_2$@COF, inset: The SEM image of TiO$_2$@COF.

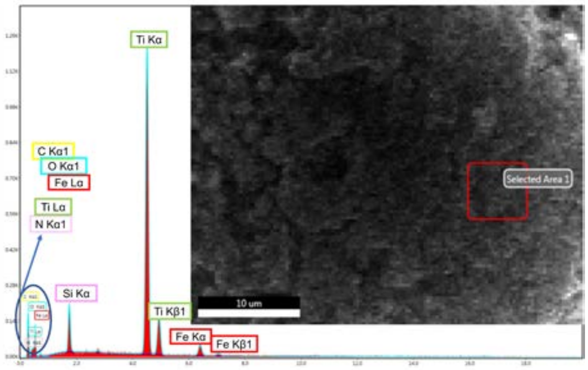


Fig. S5 The EDS spectrum of 5Fe-TiO$_2$@COF, inset: The SEM image of 5Fe-TiO$_2$@COF.

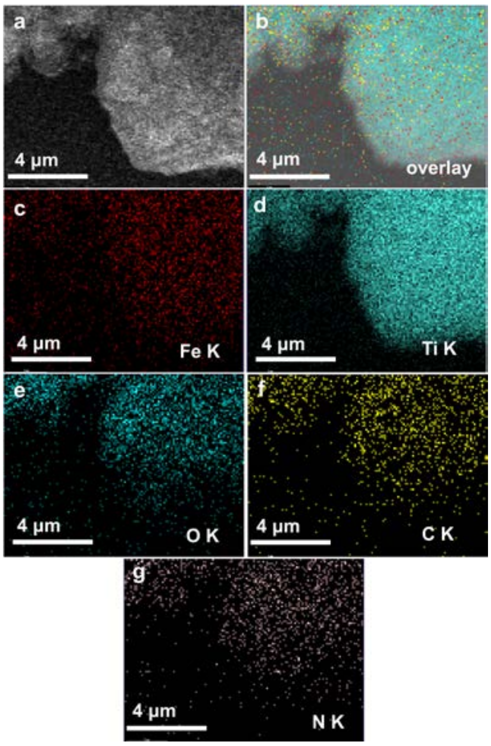


Fig. S6 The EDS mapping of 5Fe-TiO_2@COF.

5. UPS spectra of TpTa-COF and 5Fe-TiO_2

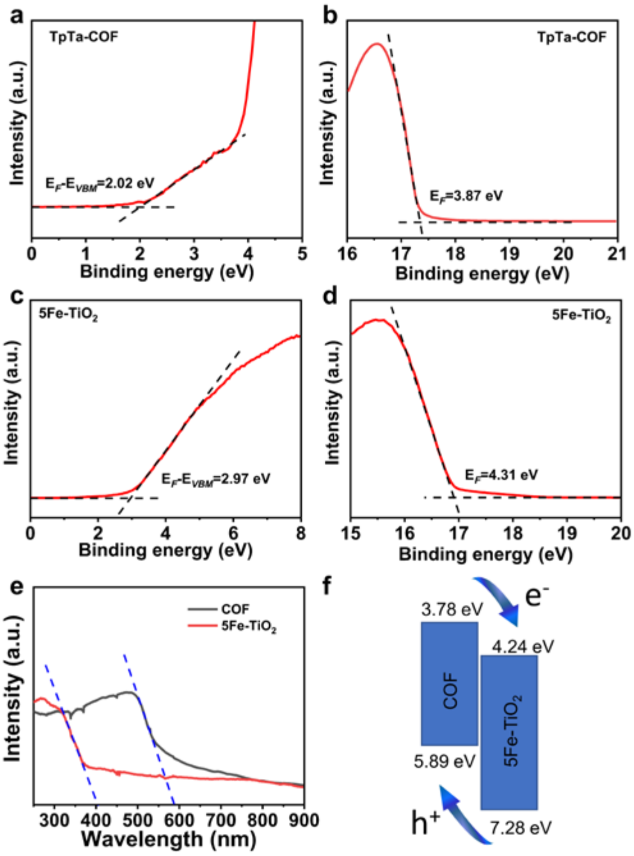


Fig. S7 The UPS spectra and the band alignment of TpTa-COF and 5Fe-TiO_2.

6. Nitrogen adsorption and desorption isotherms

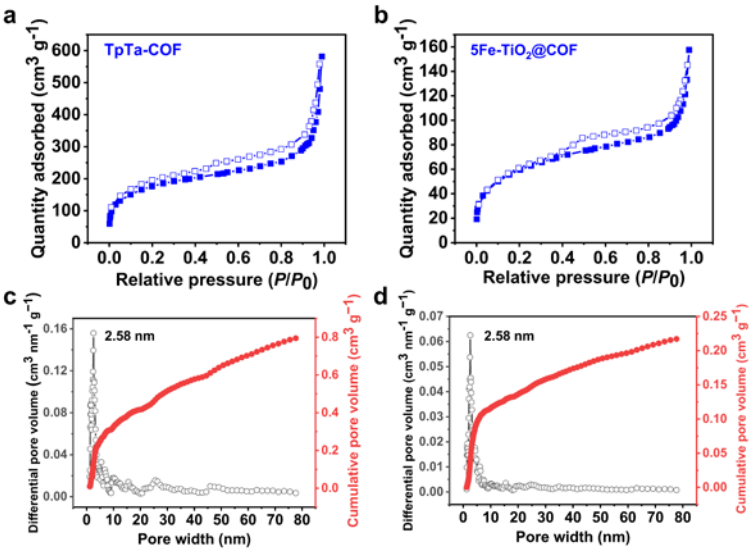
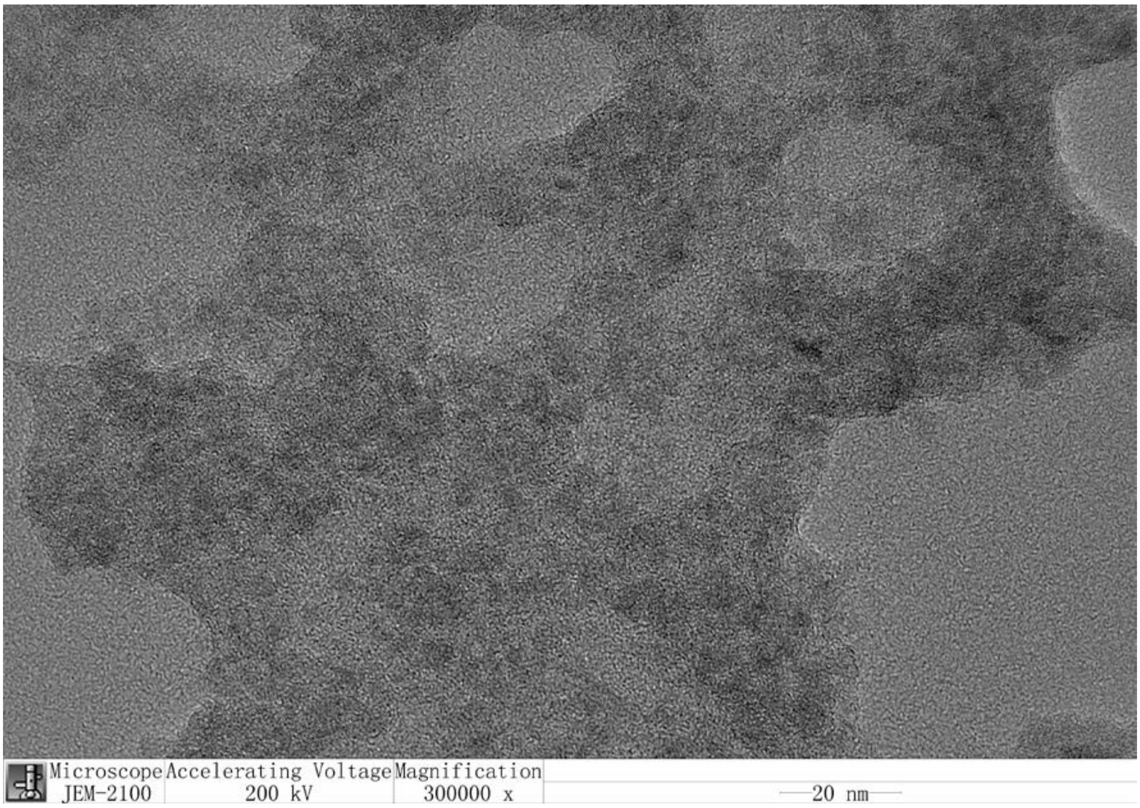


Fig. S8 The Nitrogen adsorption and desorption isotherms of TpTa-COF (a) and 5Fe-TiO_2@COF (b), DFT plots for TpTa-COF (c) and 5Fe-TiO_2@COF (d).

7. TEM images



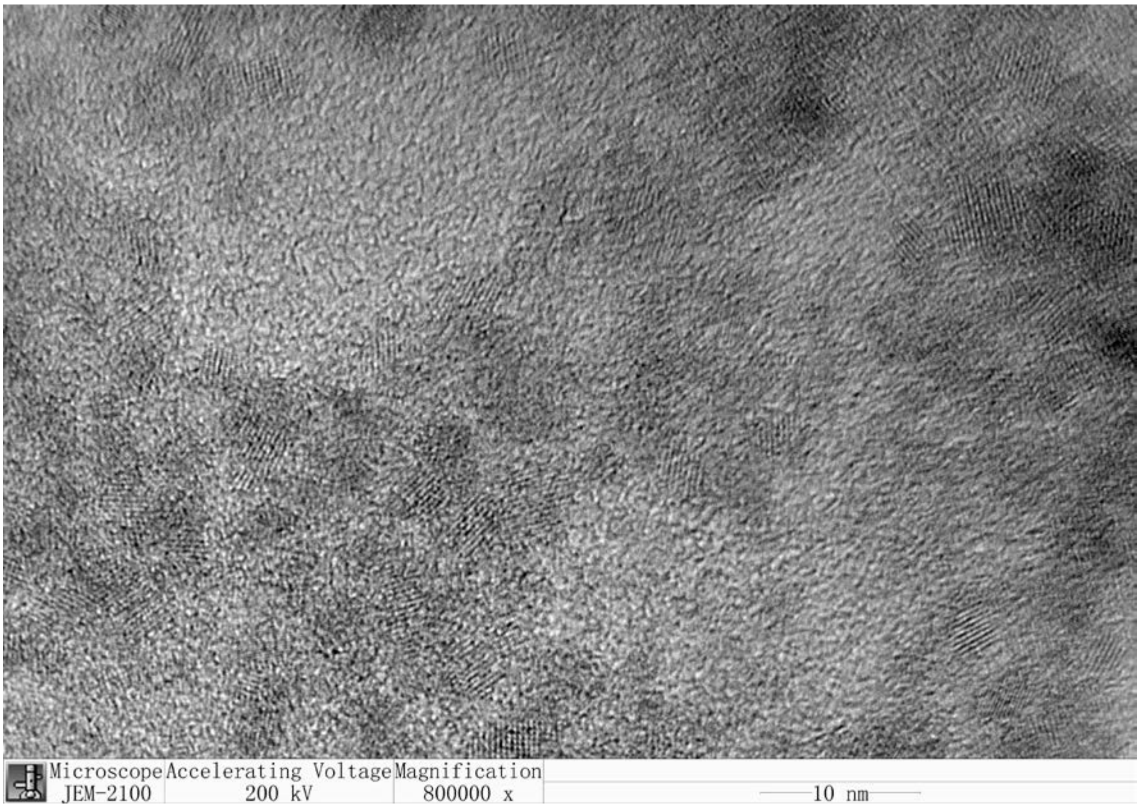


Fig. S9 The TEM images of 5Fe-TiO_2@COF.

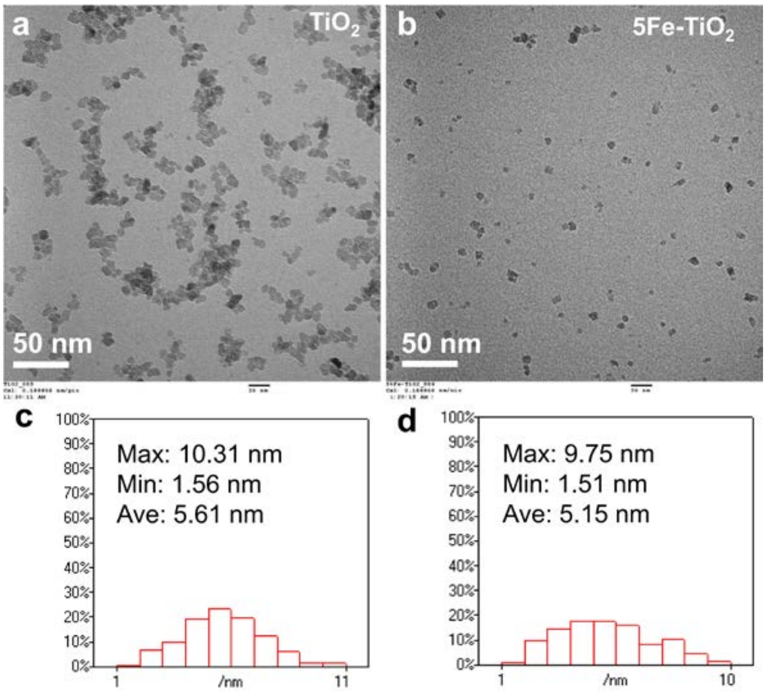


Fig. S10 The TEM images of TiO_2 (a) and 5Fe-TiO_2 (b); The size distribution of TiO_2 (c) and 5Fe-TiO_2 (d).

8. MB degradation under various light sources

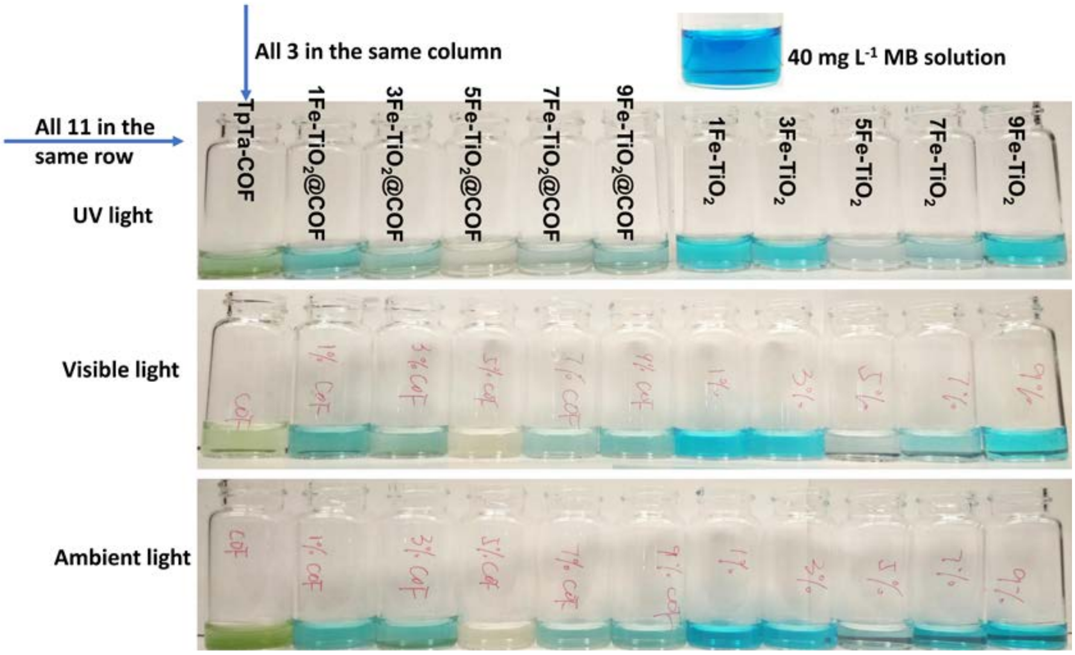


Fig. S11 Decoloration of MB samples containing various catalysts when illuminated with different light sources.

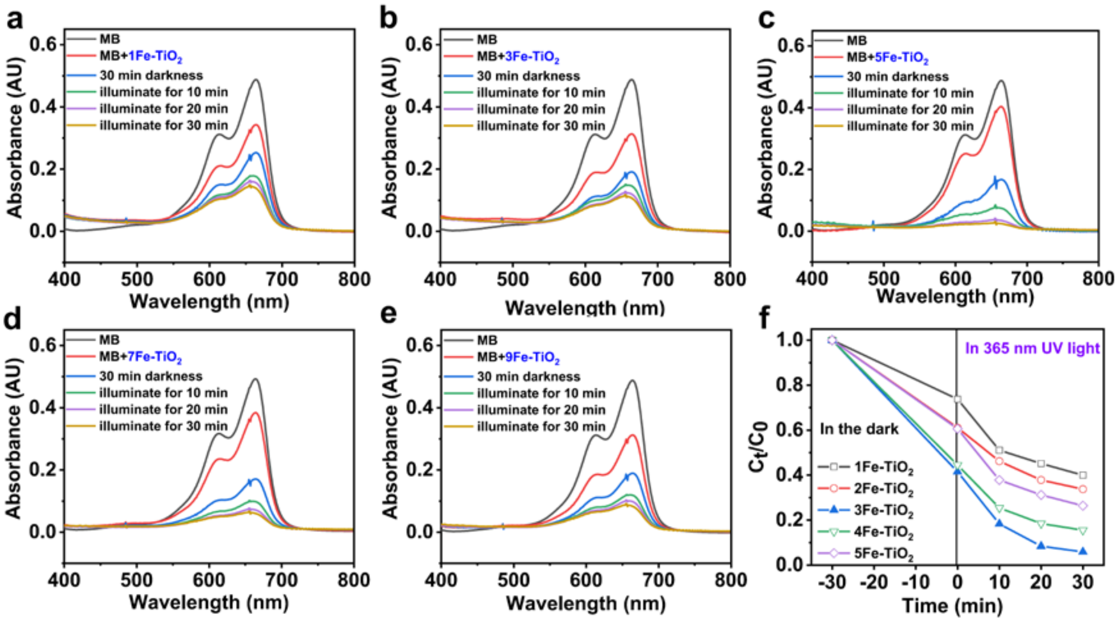


Fig. S12 The time-dependent UV-vis absorption spectra of the MB samples (40 mg L^{-1}) degraded by various catalysts (1 mg mL^{-1}, 0.4 mL): 1Fe-TiO_2 (a), 3Fe-TiO_2 (b), 5Fe-TiO_2 (c), 7Fe-TiO_2 (d) and 9Fe-TiO_2 (e); The MB degradation percentage (C_t/C_0) calculated from the figures a-e (f). An LED light (365 nm) with a power of 21 W was used as the light source.

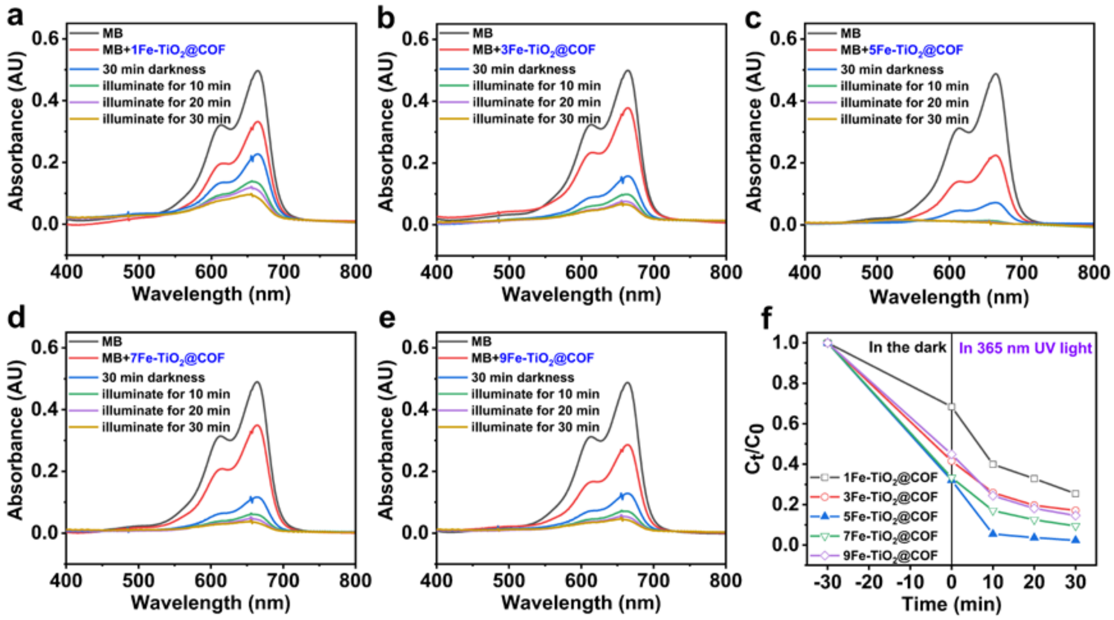


Fig. S13 The time-dependent UV-vis absorption spectra of the MB samples (40 mg L^{-1}) degraded by various catalysts (1 mg mL^{-1}, 0.4 mL): 1Fe-TiO_2@COF (a), 3Fe-TiO_2@COF (b), 5Fe-TiO_2@COF (c), 7Fe-TiO_2@COF (d) and 9Fe-TiO_2@COF (e); The MB degradation percentage (C_t/C_0) calculated from the figures a-e (f). LED light (365 nm) with a power of 21 W was used as the light source.

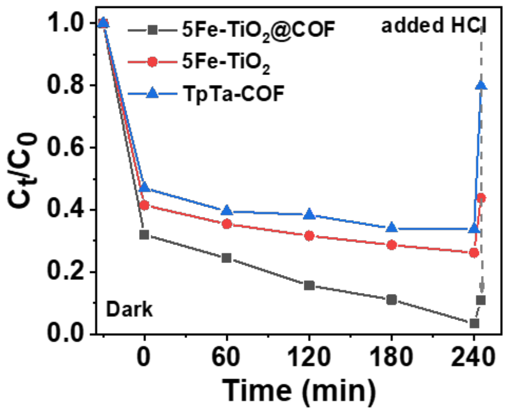


Fig. S14 The comparison of photocatalytic activity of 5Fe-TiO_2@COF, 5Fe-TiO_2 and TpTa-COF in MB (40 mg L^{-1}) degradation in the dark.

9. NMR spectra

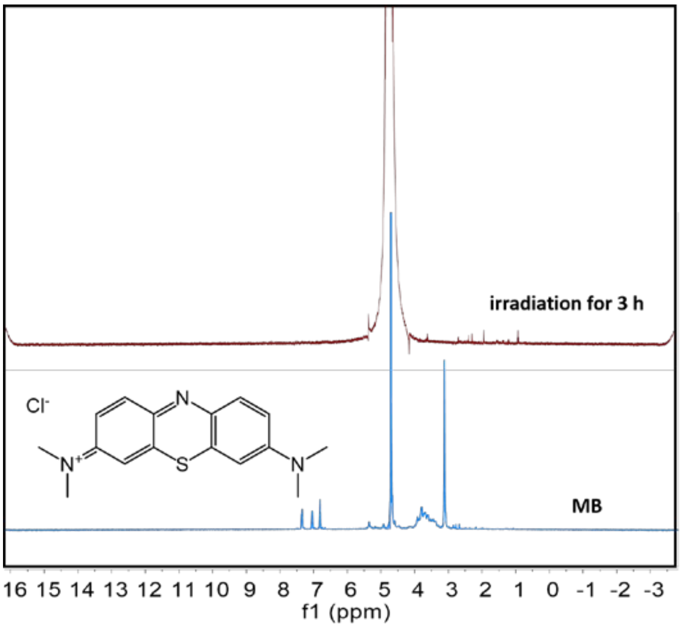


Fig. S15 The NMR spectra of 40 mg L^{-1} MB in D_2O before and after degradation in ambient light. After 3 h of degradation, the NMR spectrum does not show the peaks corresponding to MB.

10. Photoactivity comparison of TiO_2 and physically mixed COF and 5Fe-TiO_2.

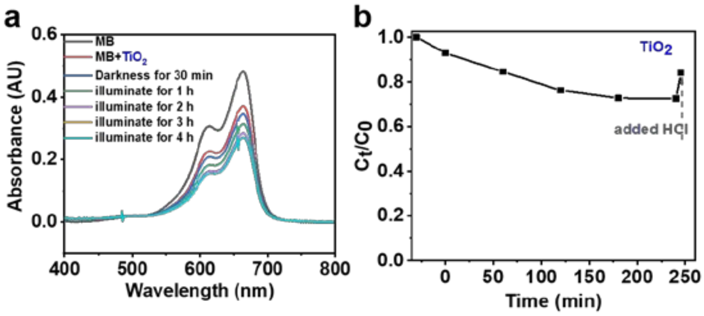


Fig. S16 The photocatalytic activity of TiO_2 under ambient light.

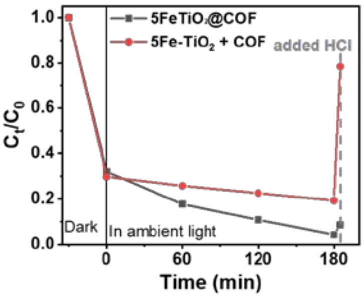


Fig. S17 The comparison of photocatalytic activity of 5Fe-TiO_2@COF and physically mixed 5Fe-TiO_2 and COF in the ambient light.

11. Reusability and stability tests of the catalysts

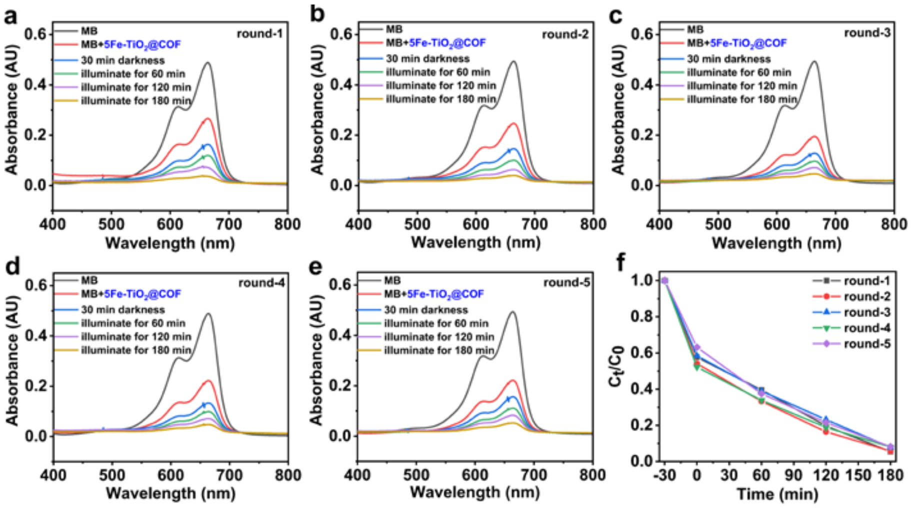


Fig. S18 The reusability test of 5Fe-TiO2@COF: the time-dependent UV-vis absorption spectra of the MB samples (40 mg L^{-1}) degraded by freshly-made 5Fe-TiO2@COF catalyst (a), and the recycled catalyst (b-e). Five consecutive runs were carried out using the recycled catalysts. After each run the catalyst was filtered and directly resubjected to a new batch of MB solution; The MB degradation percentage (C_t/C_0) calculated from Figure a-e (f). The experiments were done under ambient light without special light source.

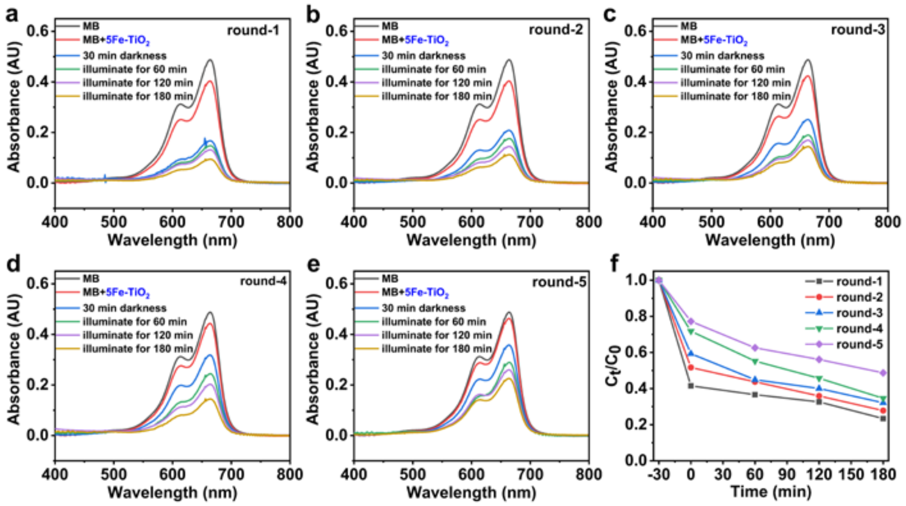


Fig. S19 The reusability test of 5Fe-TiO2: the time-dependent UV-vis absorption spectra of the MB samples (40 mg L^{-1}) degraded by freshly-made 5Fe-TiO2 catalyst (a), and the recycled catalyst (b-e). Five consecutive runs were carried out using the recycled catalysts. After each run the catalyst was filtered and directly resubjected to a new batch of MB solution; MB degradation percentage (C_t/C_0) calculated from figure a-e (f). The experiments were done under ambient light without special light source.

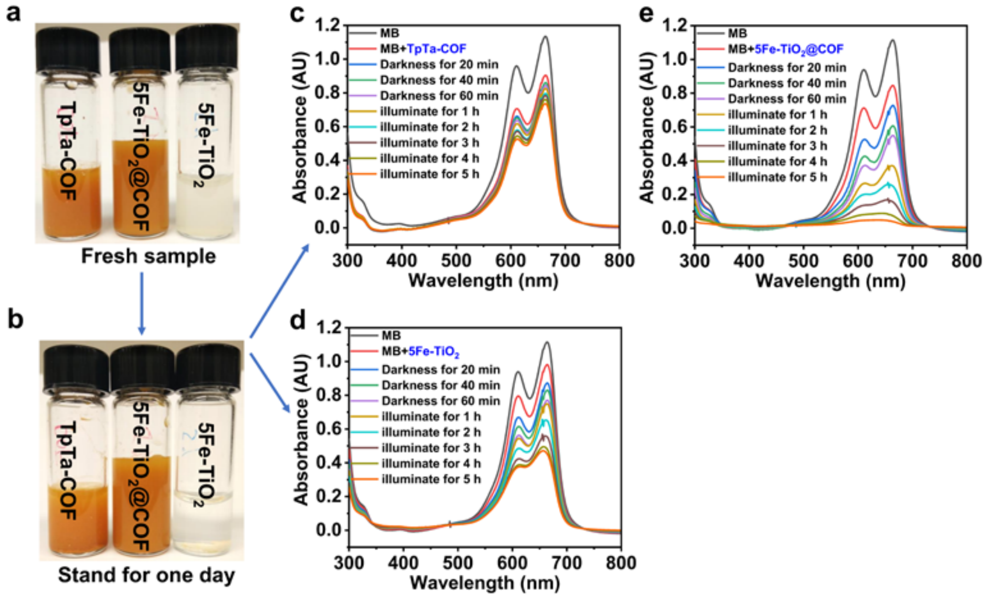


Fig. S20 The MB degradation tests using freshly-made and one-day-aged catalysts: the images of freshly made catalysts (a) and one-day-aged catalysts (b); The time-dependent UV-vis absorption spectra of the MB samples (100 mg L^{-1}) degraded by TpTa-COF (c), 5Fe-TiO_2 (d) and 5Fe-TiO_2@COF (e) under ambient light.

References

1 C. V. Yelamaggad, A. S. Achalkumar, D. S. Rao, S. K. Prasad, *J. Org. Chem.* **2009**, 74, 3168.

2 X. Han, J. Zhang, J. Huang, X. Wu, D. Yuan, Y. Liu, Y. Cui, *Nat. Commun.* **2018**, 9, 1294.