

Supporting Information

Magnetic induced construction of core-shell architecture Fe₃O₄@TiO₂-Co nanocomposites for effective photocatalytic degradation of tetracycline

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Supporting Figures:

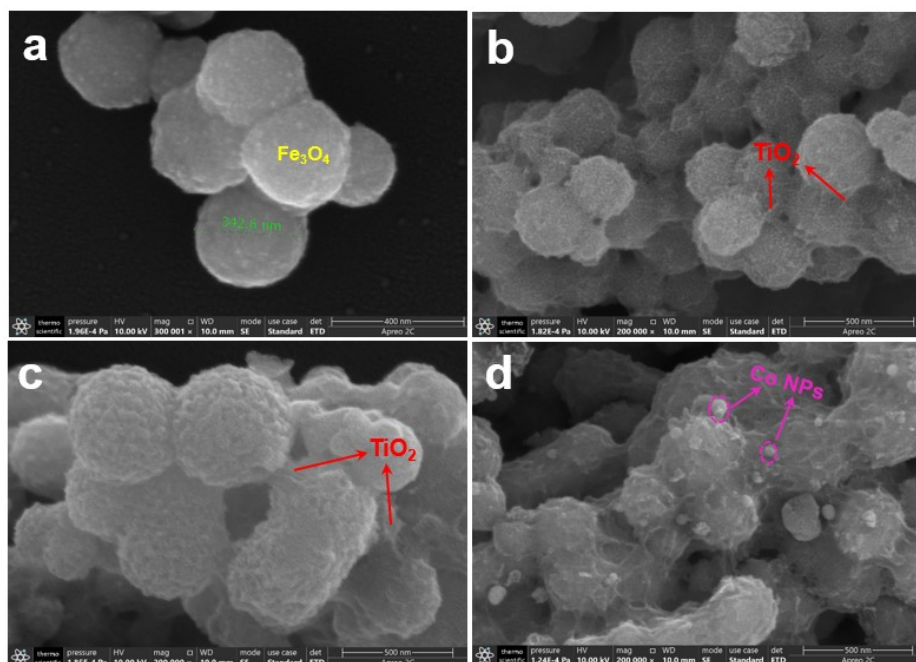


Fig. S1 SEM images of Fe₃O₄ nanospheres (a), Fe₃O₄@TiO₂ (b), Fe₃O₄@TiO₂ with a higher resolution (c) and Fe₃O₄@TiO₂-Co-2.7 (d).

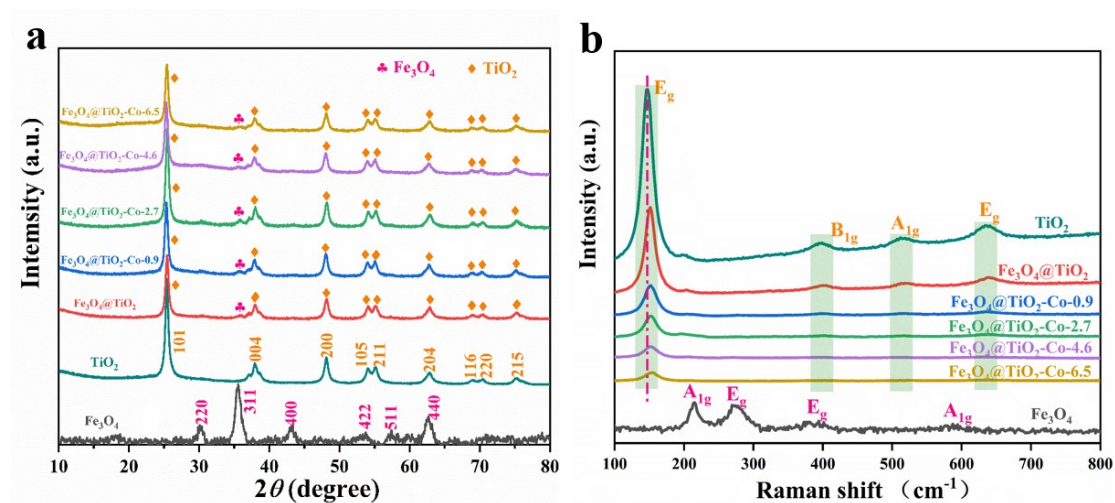


Fig. S2 X-ray diffraction patterns (a) and Raman spectra (b) of the as-prepared samples. (New supplemented data)

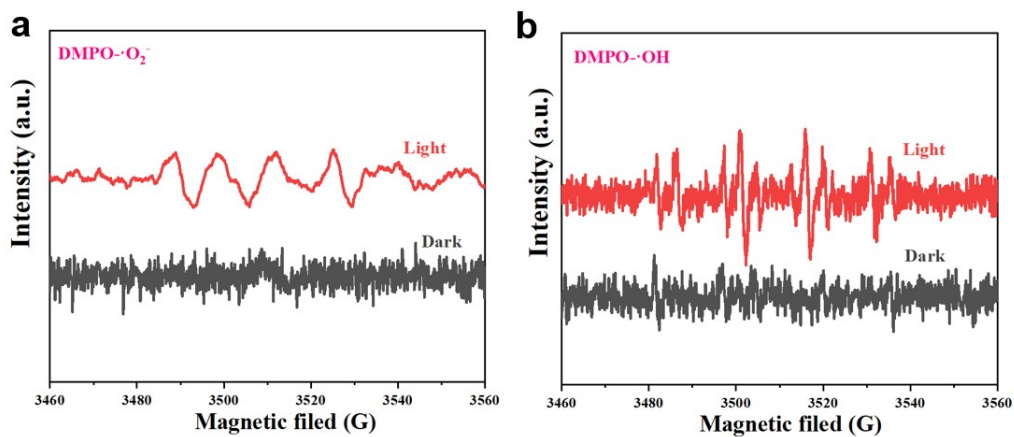


Fig. S3 Photocatalyst $\text{Fe}_3\text{O}_4@\text{TiO}_2\text{-Co-2.7}$ EPR spectra of DMPO - O_2^- (a) and DMPO - $\cdot\text{OH}$ (B) in darkness and light for 5 min.

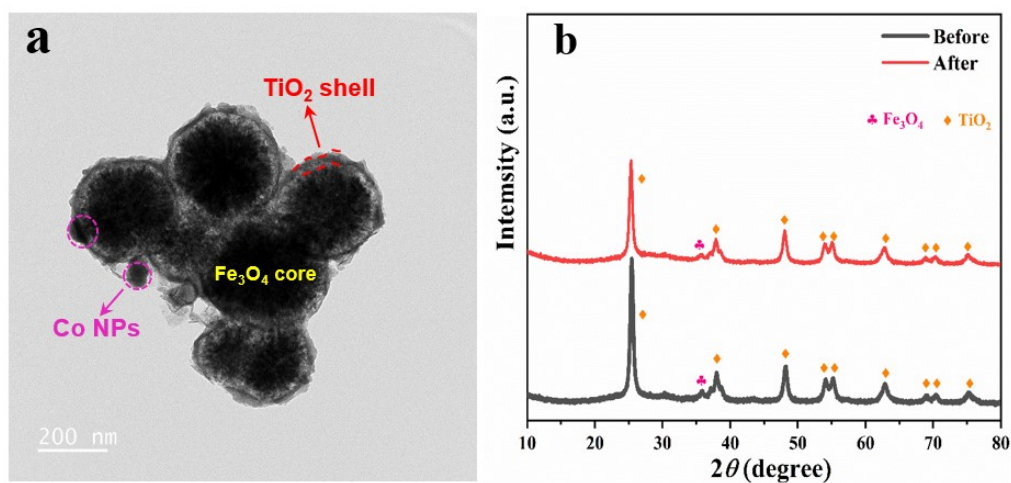


Fig. S4 TEM image (a) of the $\text{Fe}_3\text{O}_4@\text{TiO}_2\text{-Co-2.7}$ after cycling test; XRD patterns (b) of $\text{Fe}_3\text{O}_4@\text{TiO}_2\text{-Co-2.7}$ before and after cycle experiments of photocatalytic degradation of TC. (New supplemented data)

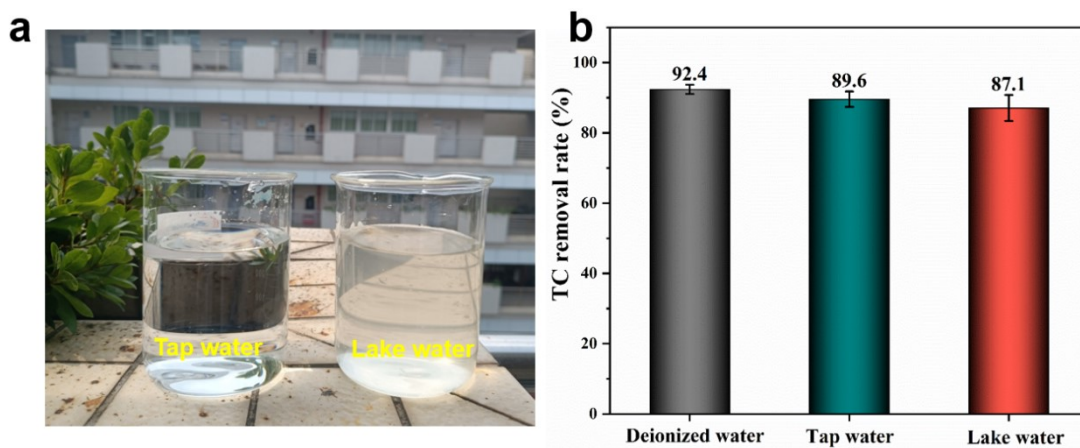


Fig. S5 (a) Photos of the as-collected water bodies (tap water and lake water); (b) Photocatalytic degradation of TC by $\text{Fe}_3\text{O}_4@\text{TiO}_2\text{-Co-2.7}$ in different water quality. (New supplemented data)

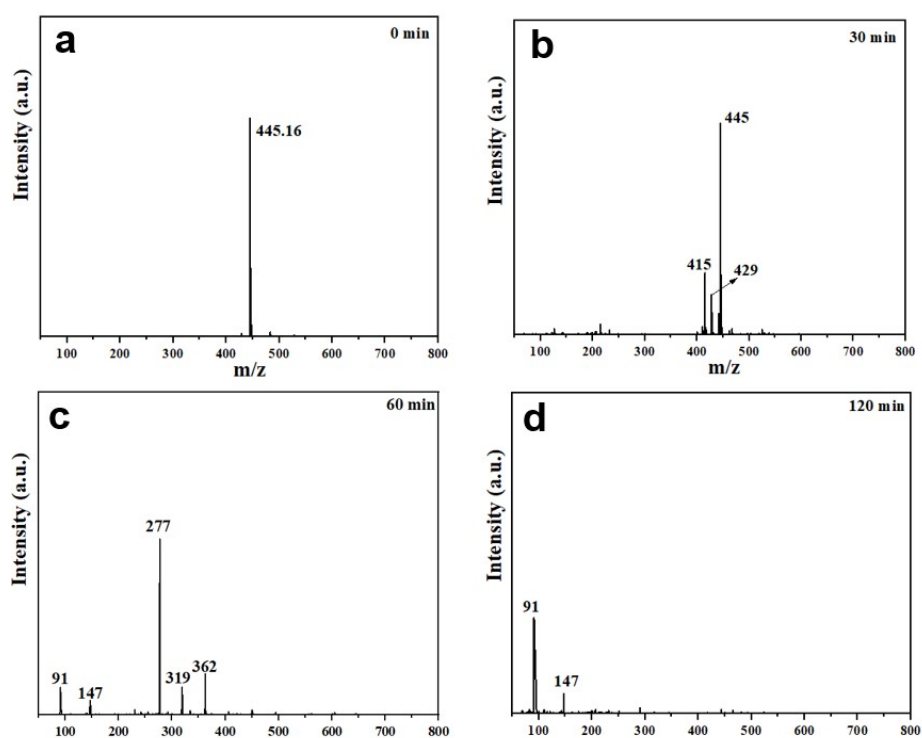


Fig. S6 The m/z of degraded TC: (a) TC in 0 min, (b) degradation of TC in 30 min, (c) 60 min and (d) 120 min. (New supplemented data)

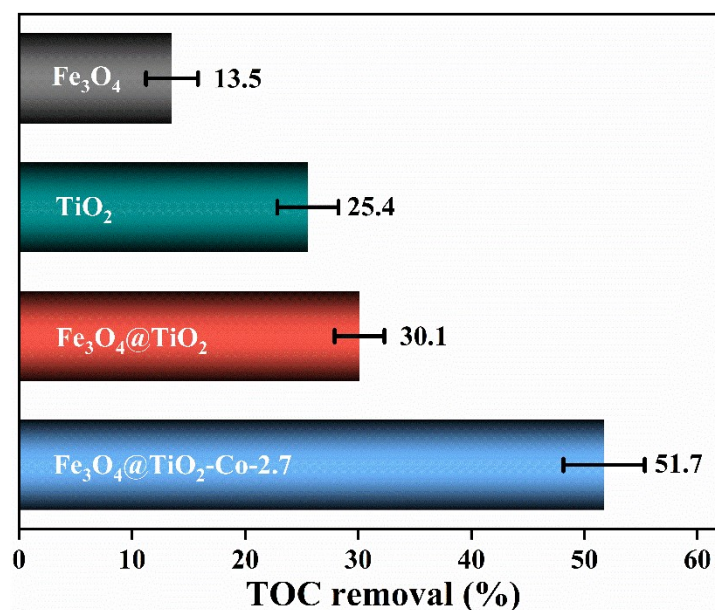


Fig. S7 Comparison of TOC removal efficiency at 120 min of reaction using Fe₃O₄, TiO₂, Fe₃O₄@TiO₂, and Fe₃O₄@TiO₂-Co-2.7. (New supplemented data)

Supporting Tables:

Table S1. The content of Co loaded on the Fe₃O₄@TiO₂-Co-x% samples was determined by ICP-OES.

| Samples | Fe ₃ O ₄ @TiO ₂ -Co-1% | Fe ₃ O ₄ @TiO ₂ -Co-3% | Fe ₃ O ₄ @TiO ₂ -Co-5% | Fe ₃ O ₄ @TiO ₂ -Co-7% |
|----------|---|---|---|---|
| Co (wt%) | 0.9 | 2.7 | 4.6 | 6.5 |

Table S2. The fitting values of the equivalent circuit elements for the various samples. (New supplemented data)

| Samples | Fitting R _s (Ω) | Fitting C _{dl} (×10 ⁻⁵ F) | Fitting R _{ct} (kΩ) |
|--|----------------------------|---|------------------------------|
| Fe ₃ O ₄ | 28.7 | 4.76 | 4.00 |
| Fe ₃ O ₄ @TiO ₂ | 23.4 | 5.83 | 3.12 |
| Fe ₃ O ₄ @TiO ₂ -Co-2.7 | 30.1 | 7.87 | 0.99 |

Table S3. Identification of the possible TC degradation products by HPLC-MS under simulated solar light irradiation. (New supplemented data)

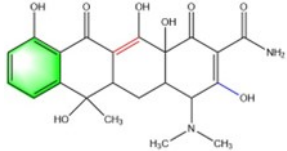
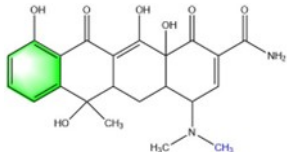
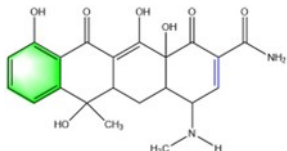
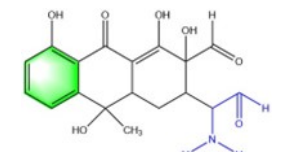
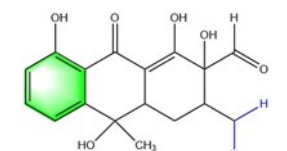
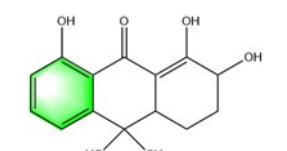
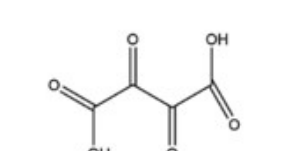
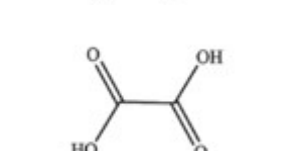
| Compounds | Formula | m/z | Proposed structure |
|-----------|----------------------|-----|---|
| TC | $C_{22}H_{24}N_2O_8$ | 445 |  |
| TC1 | $C_{22}H_{24}N_2O_7$ | 429 |  |
| TC2 | $C_{21}H_{22}N_2O_7$ | 415 |  |
| TC3 | $C_{18}H_{19}NO_7$ | 362 |  |
| TC4 | $C_{17}H_{18}O_6$ | 319 |  |
| TC5 | $C_{15}H_{16}O_5$ | 274 |  |
| TC6 | $C_4H_2O_6$ | 147 |  |
| TC7 | $C_2H_2O_4$ | 91 |  |

Table S4. The content of Co and Fe ions in reaction solution after different light radiation time was determined by ICP-MS. **(New supplemented data)**

| Sample | Light radiation time | Content of Co ions in reaction solution (mg L ⁻¹) | Content of Fe ions in reaction solution (mg L ⁻¹) |
|--|----------------------|---|---|
| Fe ₃ O ₄ @TiO ₂ - Co-2.7 | 0 | 0.0021 | 0.00037 |
| | 1 h | 0.0023 | 0.00038 |
| | 2 h | 0.0026 | 0.00041 |

Note: We investigated the content of Co and Fe ions in the solution after different reaction time (0, 1 h, and 2 h) by ICP-MS (as listed in Table S4). The results demonstrate that trace Co and Fe ions are indeed leached from samples during the process of photocatalytic reaction. The concentration of Co and Fe ions in the solution increases with prolonged time of photocatalytic reaction. It is worth noting that the content of Co and Fe leached during the photocatalytic reaction is very low.