

1. Supplementary Materials:

1.1 Figure

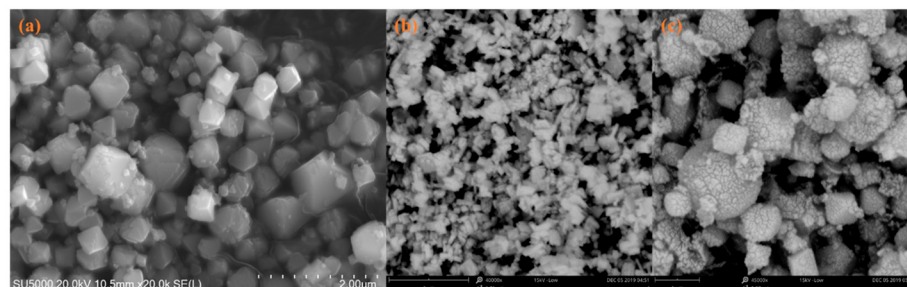


Figure S1 SEM images of (a) CoO, (b) WO₃, and (c) 70% CoO-WO₃.

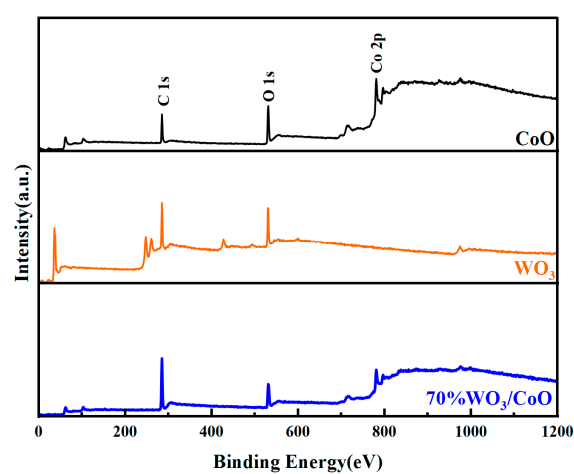


Figure S2 Survey spectra of 70% WO₃/CoO heterojunction

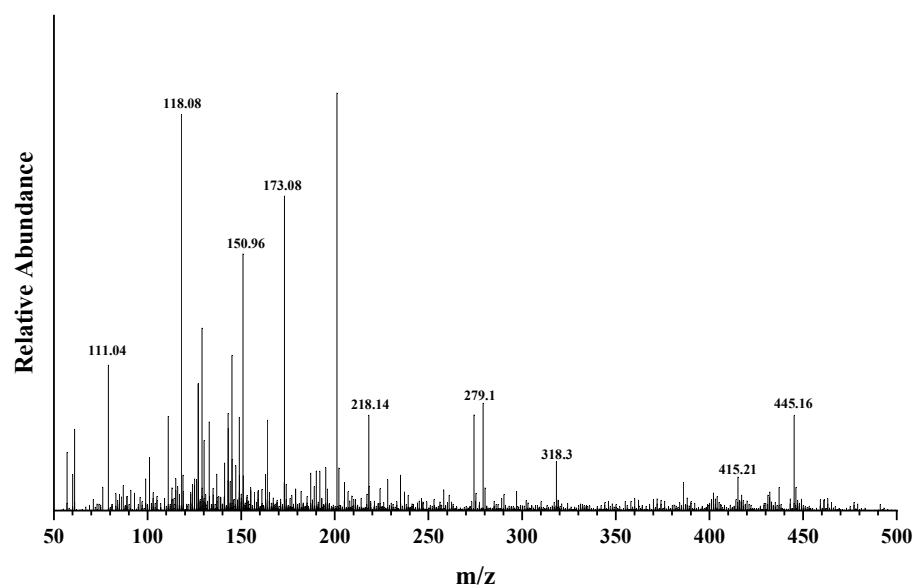


Figure S3. Mass spectra of doxycycline hydrochloride of 70% WO₃/CoO

The N₂ adsorption-desorption isotherm and pore size distribution of WO₃/CoO heterostructure are shown in Figure S4. As shown in the FigureS4(a-g), the specific surface areas of 10-90% WO₃/CoO, CoO, and WO₃ photocatalysts are 13.036045 m²g⁻¹, 14.685631 m²g⁻¹, and 15.356614 m²g⁻¹,

10.472091 m^2g^{-1} , 8.672618 m^2g^{-1} , 4.170520 m^2g^{-1} , and 8.635148 m^2g^{-1} , respectively. The pore volumes were 0.322932 cm^3g^{-1} , 0.169603 cm^3g^{-1} , 0.149632 cm^3g^{-1} , 0.073650 cm^3g^{-1} , 0.050435 cm^3g^{-1} , 0.034203 cm^3g^{-1} , 0.248725 cm^3g^{-1} , and the pore sizes were 83.125136 nm, 41.909145 nm, 34.841508 nm, 25.984281 nm, and 22.586335 nm, respectively. This result is closely related to the morphology of the material. WO_3 adheres to octahedral CoO , significantly improving the specific surface area of WO_3/CoO composites. The adsorption properties of the materials are closely related to the specific surface area. As shown in Figure S4(h-i), the adsorption performance of WO_3/CoO for TC and Cr (VI) positively correlates with the specific surface area. It can be seen that the adsorption performance of WO_3/CoO decreased significantly after 30 min, and the adsorption equilibrium was reached. However, the material can only adsorb a few pollutants, and the removal of pollutants mainly depends on the excellent photocatalytic performance of the material, which is also confirmed by the photocatalytic experiment and mechanism.

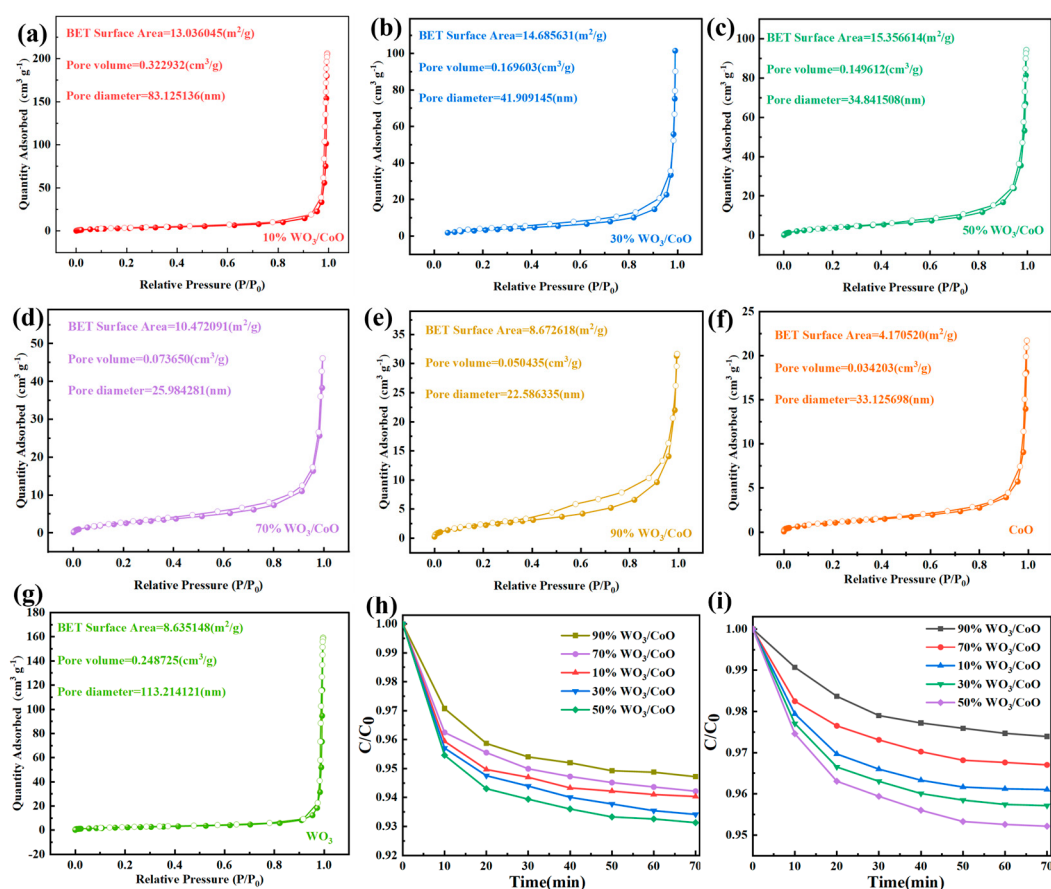


Figure S4 Nitrogen adsorption-desorption isotherm and pore size distribution curve (a-e) 10-90% WO_3/CoO , (f) CoO , (g) WO_3 ; Dark adsorption experiment (h) TC, (i) Cr (VI).

Figure S5(a) shows the TEM image of 70% WO_3/CoO . As shown in the Figure S5(a), granular WO_3 package the surface of octahedral CoO , forming a 70% WO_3/CoO heterojunction, which can provide more photocatalytic reaction sites and further improve photocatalytic activity. Figure S5(b) shows the HRTEM image of 70% WO_3/CoO . The clear stripes indicate that the lattice spacing of nanoparticles is 0.25 nm, which is consistent with the (111) crystal plane of CoO . At the same time, the lattice stripes with a spacing of 0.21 nm can be observed, corresponding to the (202) crystal plane of WO_3 . Subsequently, energy dispersive X-ray (EDX) analysis of 70% WO_3/CoO showed (Figure S5 (c-f)) that Co and some O were derived from CoO , while the main element W and some O were derived from WO_3 . Co, W, and O are evenly distributed in the 70% WO_3/CoO heterojunction. Therefore, the 70% WO_3/CoO p-n heterojunction was successfully synthesized.

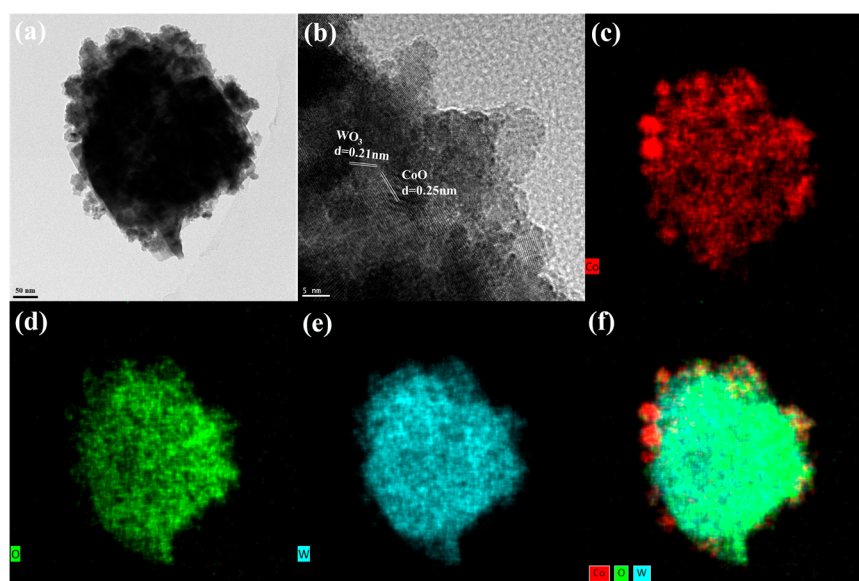


Figure S5 (a-b) TEM and HRTEM images of 70% WO_3/CoO ; (c-f) EDX mapping of 70% WO_3/CoO

As shown in Figure S6(a), the TEM image shows that the morphology and structure of 70% WO_3/CoO have not changed significantly after the photocatalytic reaction, and the granular WO_3 is still wrapped on the surface of octahedral CoO , showing excellent structural stability. Through XRD (Figure S6(b)), it can be seen that 70% WO_3/CoO after the reaction still exhibits the characteristics of CoO and WO_3 monomers, and there is no significant change compared to before the reaction, further proving that the morphology and structure of 70% WO_3/CoO have excellent stability.

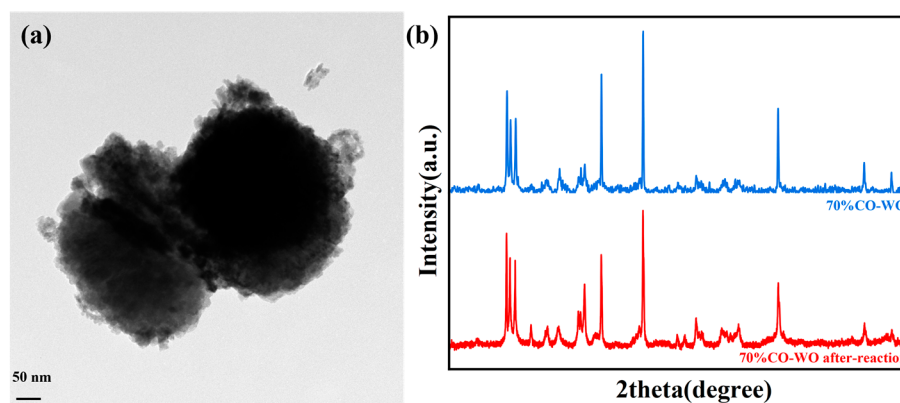


Figure S6 (a) TEM images, (b) XRD of 70% WO_3/CoO after the photocatalytic process

The band gaps of 10-90% WO_3/CoO composite materials were calculated using the Tauc Plot equation, and the band gaps of the composite materials were 2.59, 2.33, 2.10, 1.94, and 1.87 eV, respectively.

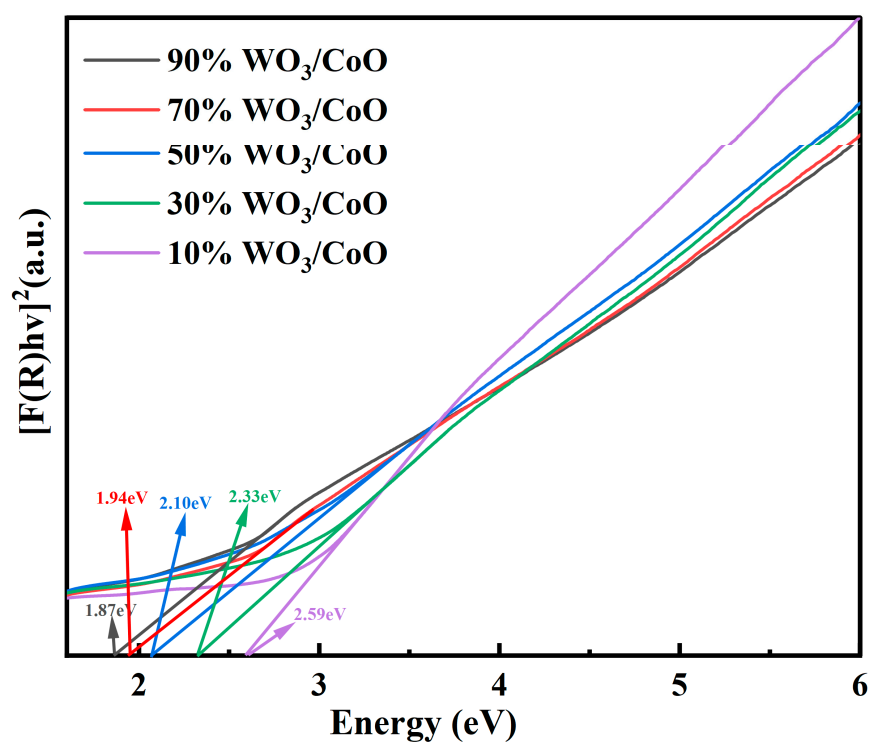
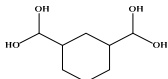
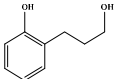
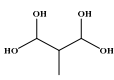


Figure S7 10-90% WO₃/CoO composite material bandgap

Table S1 Possible intermediate products

Product	Chemical Formula	Specific Charge(m/z)	Structure
TC	C ₂₂ H ₂₄ N ₂ O ₈	445	
P1	C ₂₀ H ₂₀ N ₂ O ₈	416	
P2	C ₁₇ H ₁₈ O ₆	318	
P3	C ₁₈ H ₂₁ O ₄ N	318	
P4	C ₁₅ H ₁₆ O ₅	279	
P5	C ₁₄ H ₂₀ O ₂	218	

P6	$C_8H_{12}O_4$	173	
P7	$C_9H_{10}O_2$	149	
P8	$C_6H_8O_2$	111	
P9	$C_4H_6O_4$	118	

1.3 Material performance comparison

By comparing with other materials, it further proves the performance advantages of 70% WO_3/CoO composite photocatalyst. Shi et al. [1] prepared CoO octahedra decorated with carbon quantum dots for the degradation of tetracycline (TC) in water, with a final removal rate of 87%, significantly lower than 95.35% of 70% WO_3/CoO . The micro-nano spherical $CoO/BiVO_4$ p-n heterojunction photocatalyst prepared by Wang et al. [2] also exhibited excellent photocatalytic performance against TC (87.3%, 90 minutes). Still, it was also lower than 95.35% of 70% WO_3/CoO . The S-scheme $WO_3/CdIn_2S_4$ photocatalyst prepared by Chen et al. [3] can degrade 90% of TC, demonstrating excellent photocatalytic performance but only staying at the level of a single pollutant. Lu et al. [4] conducted research on the removal of mixed pollutants and found that the Z-Scheme type CoO/Bi_2WO_6 p-n heterojunction can achieve synchronous removal of TC and Cr (VI), with removal rates of 90.7% and 57.5%, respectively, still lower than 95.35% and 70.2% of 70% WO_3/CoO .

[1] Shi, W.; Guo, F.; Wang, H.; Han, M.; Li, H.; Yuan, S.; Huang, H.; Liu, Y.; Kang, Z. Carbon dots decorated the exposing high-reactive (111) facets CoO octahedrons with enhanced photocatalytic activity and stability for tetracycline degradation under visible light irradiation. *Appl. Catal. B Environ.* 2017, 219, 36–44.

[2] Wang, S.; Zhao, L.; Huang, W.; Zhao, H.; Chen, J.; Cai, Q.; Jiang, X.; Lu, C.; Shi, W. Solvothermal synthesis of $CoO/BiVO_4$ p-n heterojunction with micro-nano spherical structure for enhanced visible light photocatalytic activity towards degradation of tetracycline. *Mater. Res. Bull.* 2021, 135, 111161.

[3] Pei, C.Y.; Chen, Y.G.; Wang, L.; Chen, W.; Huang, G.B. Step-scheme $WO_3/CdIn_2S_4$ hybrid system with high visible light activity for tetracycline hydrochloride photodegradation. *Appl. Surf. Sci.* 2021, 535, 147682.

[4] Lu, C.Y.; Yang, D.Q.; Wang, L.T.; Wen, S.J.; Cao, D.L.; Tu, C.Q.; Gao, L.N.; Li, Y.L.; Zhou, Y.H.; Huang, W. Facile construction of CoO/Bi_2WO_6 p-n heterojunction with following Z-Scheme pathways for simultaneous elimination of tetracycline and Cr(VI) under visible light irradiation. *J. Alloys Compd.* 2022, 904, 164046.