Electronic Supplementary Information

Fabrication of ZC-bimetallic MOF derived ZCO/Co_3O_4 by different zinc source anions and the effect of photocatalytic performance

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S1. Chemical reagents

Zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$) was procured from Tianjin Fuchen Chemical Reagents Factory. Zinc acetate tetrahydrate ($Zn(CH_3COO)_2·4H_2O$) was procured from Tianjin Deen Chemical Reagent Co., LTD. Zinc sulfate heptahydrate ($ZnSO_4·7H_2O$) was procured from Aladdin-e, methanol was procured from Tianjin Fuyu Fine Chemical Co., Ltd. Zinc chloride hexahydrate ($ZnCl_2·6H_2O$), 2-methylimidazole (2-MeIM) and cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$) were supplied by Macklin. All of these analytical-grade chemical reagents were utilized just as supplied, requiring no further purification.

S2. Photoelectrochemical testing conditions

The photoelectrochemical tests were performed on a Shanghai Chenhua CHI660C electrochemical workstation equipped with a three-electrode system. The Pt sheet electrode and saturated calomel electrode were used as the counter electrode and reference electrode, respectively, while the working electrode was ITO glass modified with the photocatalyst. The electrolyte solution was Na_2SO_4 solution (0.5 mol/L). The pH of the electrolyte solution is close to 7.

(a) Transient photocurrent measurement (i-t curve)

For the test, the current-time (i-t) curve option was selected. The initial potential was set to the open-circuit potential, and the light source was a 300 W xenon lamp, with the light switched on and off every 20 seconds.

(b) Electrochemical impedance spectroscopy (EIS)

For the test, the AC impedance option was selected. The measurement was performed under open-circuit voltage with a voltage amplitude of 5 mV, and the scan range was 0.01 to 100,000 Hz.

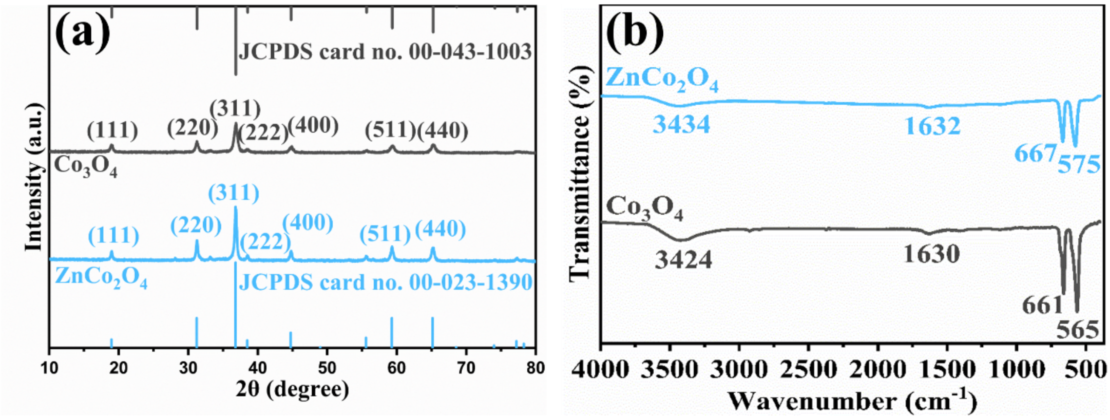

Fig. S1 XRD patterns (a) and FTIR spectrum (b) of $ZnCo_2O_4$ and Co_3O_4.

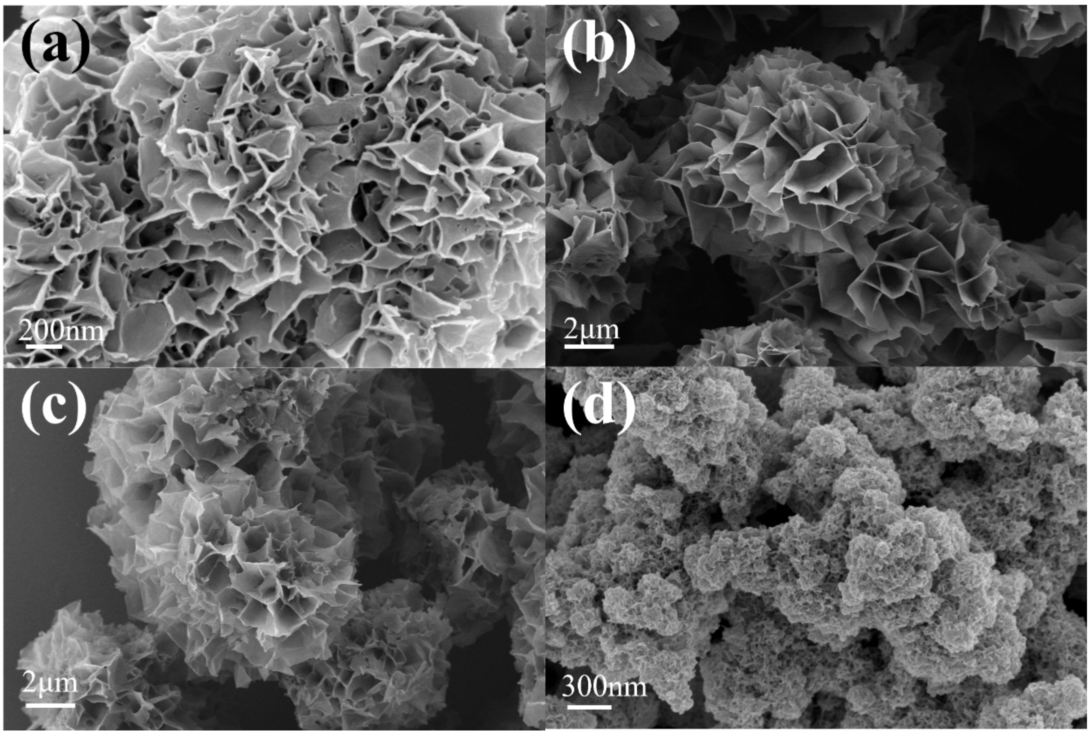

Fig. S2 SEM images of ZC-MOF: C-ZCO/Co_3O_4 precursor (a), A-ZCO/Co_3O_4 precursor (b), N-ZCO/Co_3O_4 precursor (c) and S-ZCO/Co_3O_4 precursor (d).

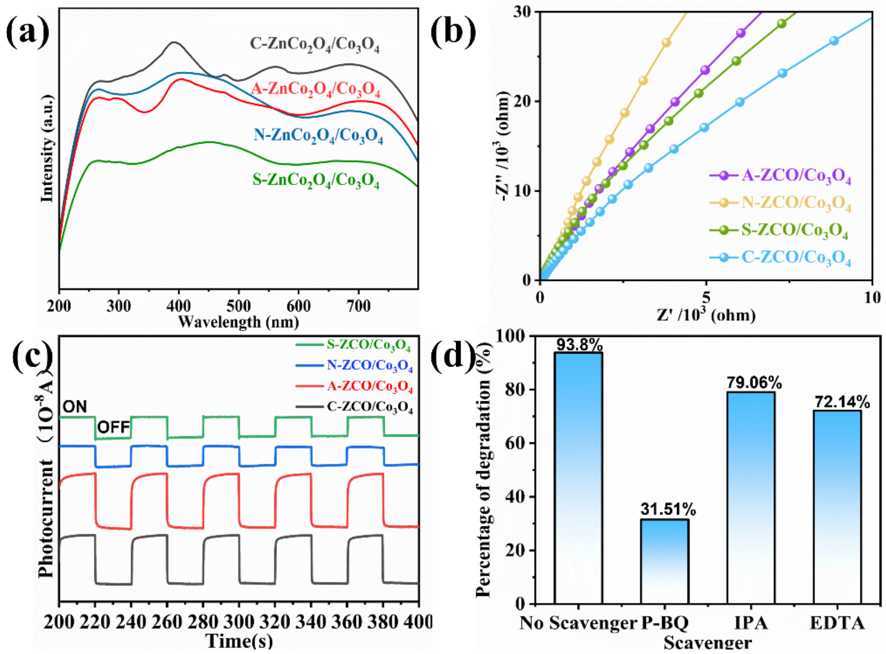

Fig. S3 UV–vis DRS diffuse reflection absorption spectra and tauc plot for the samples (a); Electrochemical impedance spectroscopy of different ZCO/Co_3O_4 photocatalysts (b); Intermittent photocurrent response (c) and effect of distinct scavengers (d).

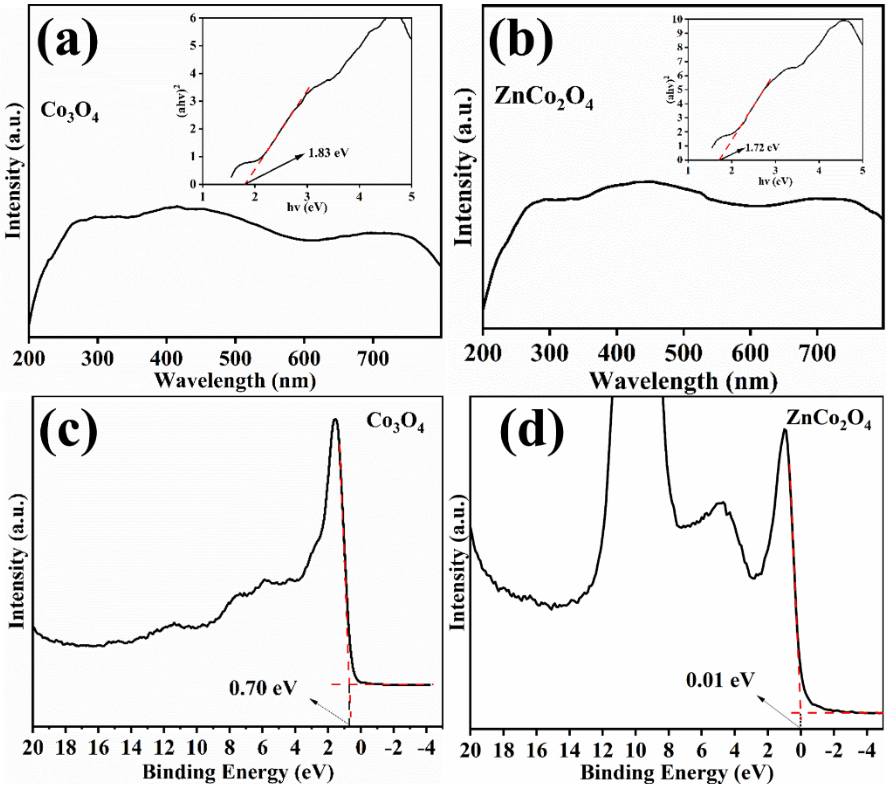

Fig. S4 UV-Vis diffuse reflectance spectra diagrams of Co_3O_4 (a, inset: plots of $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^2$ versus photo energy (hv)) and UV-Vis diffuse reflectance spectra diagrams of $ZnCo_2O_4$ (b, inset: plots of $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^2$ versus photo energy (hv));
The VB-XPS spectra of Co_3O_4 (c) and $ZnCo_2O_4$ (d)

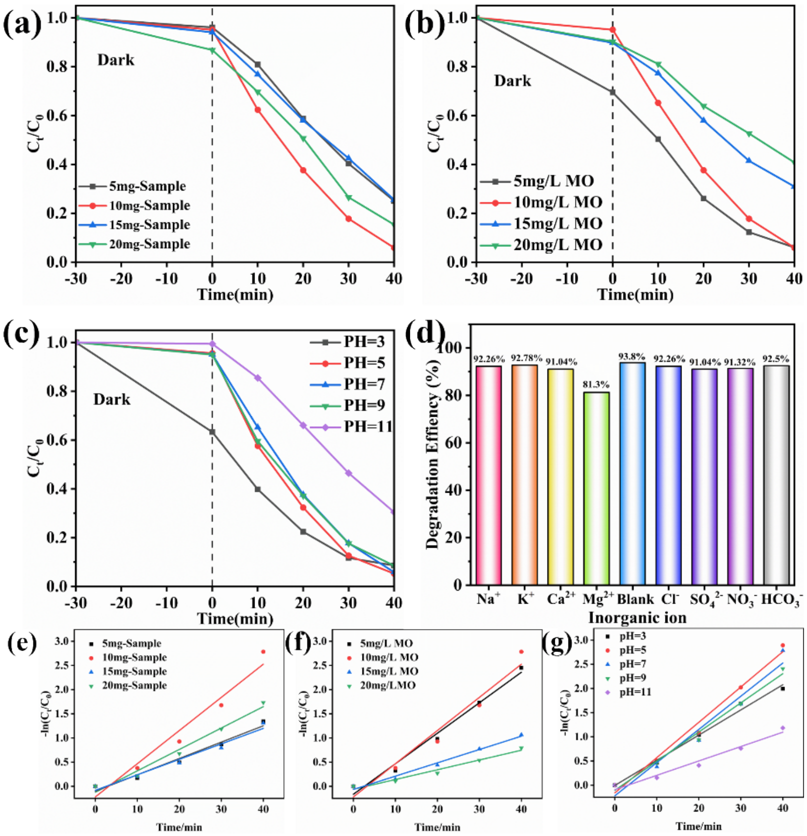

Fig. S5 Photocatalytic degradation efficiency of MO under different conditions: different catalyst loading amounts (a); Different concentrations of MO (b); Different pH values (c); Different inorganic ions (d); And equivalent pseudo-first-order Langmuir-Hinshelwood relationship for MO degradation under different conditions (e-g)

Fig. S5a illustrates the effect of different C-ZCO/Co_3O_4 loading amounts on the degradation removal rate of 10 mg/L Methylene Orange wastewater. In the experiment, four different loading amounts of 5 mg, 10 mg, 15 mg, and 20 mg were selected for the study. As shown in the figure, with the increase in material loading, the photocatalytic degradation efficiency gradually increased, followed by a brief decrease and then a rise again. The degradation efficiencies for the four loading amounts were 74%, 93.7%, 72.9%, and 82.3%, respectively. When the C-ZCO/Co_3O_4 loading reached 10 mg, the removal rate of Methylene Orange was nearly 94%. However, it is noteworthy that when the loading amount exceeded 10 mg, the degradation efficiency began to decline. This could be because an excessive amount of C-ZCO/Co_3O_4 interferes with light absorption and may lead to the mutual consumption of free radicals. Fig. S5e shows the first-order kinetic curve for the degradation of Methylene Orange by C-ZCO/Co_3O_4, where the slope of the kinetic curve at 10 mg loading is the largest, indicating the fastest degradation rate at this loading. The degradation rates of tetracycline for different C-ZCO/Co_3O_4 loading amounts were 0.034 min^{-1}, 0.068 min^{-1}, 0.032 min^{-1}, and 0.044 min^{-1}, respectively. In addition, the correlation coefficients for the first-order kinetic fitting were all above 0.9, demonstrating excellent correlation.

Fig. S5b presents the degradation performance of C-ZCO/Co_3O_4 at different Methylene Orange concentrations. The concentration range investigated was from 5 mg/L to 20 mg/L. As shown in the figure, with the increase in Methylene Orange concentration, the photocatalytic degradation efficiency gradually decreased, with the specific degradation efficiencies being 91.3%, 94%, 65.58%, and 54.82%, respectively. Fig. S5f shows the first-order kinetic fitting curve for the degradation of Methylene Orange by C-ZCO/Co_3O_4, where the 10 mg/L concentration of Methylene Orange wastewater exhibited the fastest degradation rate. The degradation rates for different concentrations of Methylene Orange were 0.063 min^{-1}, 0.068 min^{-1}, 0.027 min^{-1}, and 0.020 min^{-1}, respectively. The high concentration of Methylene Orange may occupy the surface of ZCO/Co_3O_4, reducing the number of effective active sites and leading to a decrease in degradation efficiency. The kinetic fitting results show good correlation, with correlation coefficients exceeding 0.94.

The pH of the solution is one of the key factors affecting photocatalytic performance. Under different pH values, organic pollutants may exist in different forms, and the surface potential of the photocatalyst will also change with pH. To further explore the degradation efficiency of C-ZCO/Co_3O_4 for methyl orange (MO) under different pH conditions, photocatalytic experiments were conducted within the pH range of 3, 5, 7, 9, and 11. As shown in Fig. S5c, the corresponding removal rates at pH = 3, 5, 7, 9, and 11 were 86.38%, 94.46%, 94%, 91.02%, and 69.38%, respectively. The results show that, in highly acidic conditions, due to the high concentration of H^+, the adsorption capacity of MO is enhanced, but the degradation efficiency is reduced. This is likely because acidic conditions increase the solubility of MO in water, making it easier to diffuse to the catalyst surface and increasing contact opportunities, which in turn enhances the adsorption rate. However, the high adsorption rate causes MO to occupy the active sites of the catalyst, hindering the generation of oxidative radicals, thus leading to a decrease in photocatalytic degradation efficiency. On the contrary, in alkaline conditions, the higher concentration of OH^- suppresses the adsorption of MO, and the pollutants cannot be effectively adsorbed on the catalyst surface. The contact opportunities between photogenerated carriers (electrons and holes) and pollutants are reduced, resulting in lower reaction efficiency. Considering all factors, a slightly neutral environment is more favorable for the interaction between active species (such as superoxide radicals and holes) and organic pollutants. Fig. S5g presents the first-order kinetic curves for Methylene Orange degradation under different pH conditions, which are 0.052 min^{-1}, 0.073 min^{-1}, 0.069 min^{-1}, 0.060 min^{-1}, and 0.029 min^{-1}, respectively. Through first-order kinetic fitting analysis, the correlation coefficients are all greater than 0.94, indicating excellent correlation between the data.

Additionally, the inorganic ions present in wastewater, due to their different charges, can have a certain impact on the degradation process of pollutants. Inorganic ions can react with free radicals in the reaction system, thereby changing the concentration and activity of the free radicals, which in turn affects the degradation process of organic pollutants. Therefore, the effects of Cl^-, NO_3^-, SO_4^{2-}, HCO_3^-, Na^+, Mg^{2+}, Ca^{2+}, and K^+ on the photocatalytic degradation of Methylene Orange by C-ZCO/Co_3O_4 were investigated. As shown in Fig. S5d, the anions such as Cl^-, NO_3^-, and SO_4^{2-} had no significant impact on the degradation of Methylene Orange in this system. Even in the presence of these anions, the degradation efficiency remained above 90%. Ca^{2+} and K^+, as monovalent or divalent cations, do not typically participate directly in oxidation-reduction reactions during the photocatalytic process. This means they do not react with photo-generated electrons or holes, nor do they react significantly with the generated active species (such as hydroxyl radicals). Therefore, they do not directly promote or inhibit the degradation of Methylene Orange. Furthermore, due to the smaller ionic radii and lower charge density of these ions, they are less likely to occupy a large number of active sites or alter the electronic structure of the catalyst. As a result, their impact on the catalyst activity is minimal.

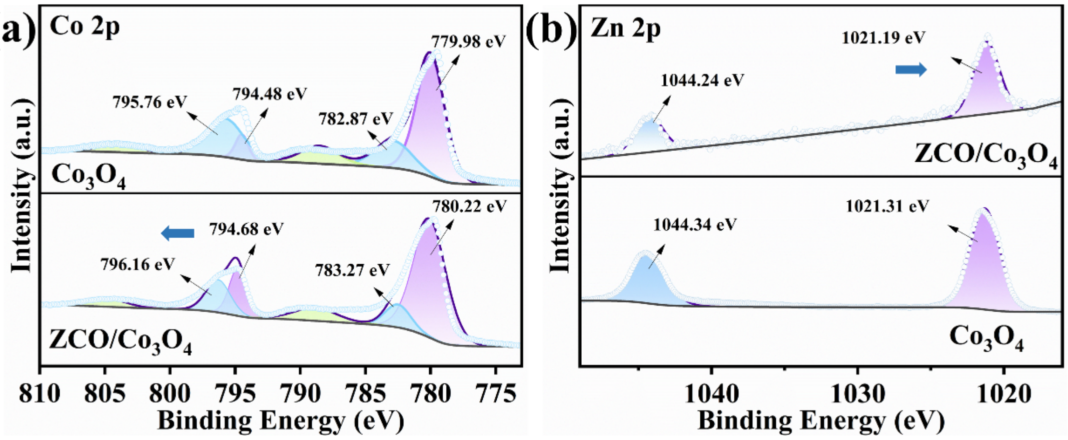

Fig. S6 XPS spectra of Co 2p and Zn 2p for ZCO/Co_3O_4 composite, Co_3O_4, and ZCO

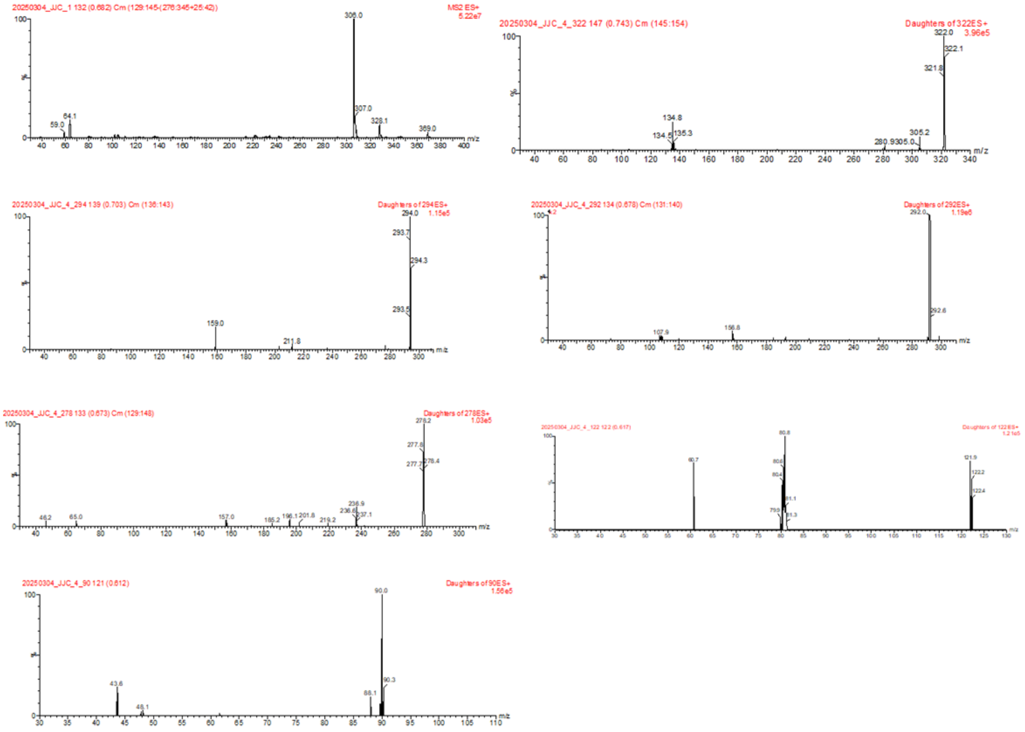

Fig. S7 The degradation spectrum of MO (LCMS).