

Supporting Information

Co/ZnO/C Heterostructured Nanowires Derived from Layered Hydroxides: Magnetically Recyclable Photocatalysts for Efficient Tetracycline Degradation

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Experimental

1.1 Materials

Tetracycline (TC), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, sodium salicylate ($\text{C}_7\text{H}_5\text{NaO}_3$, NaHSal), NaOH, benzoquinone (BQ), isopropyl alcohol (IPA), and triethanolamine (TEOA) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). All chemicals were analytical grade and used as received without further purification.

1.2 Synthesis of $\text{ZnCo}_x\text{-Sal}$ LHRs precursor

In a typical synthesis, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 150 mL deionized (DI) water at a molar ratio of 9:1 to prepare a 1.0 mol L^{-1} mixed solution. The above solution was then thoroughly mixed with 150 mL 2.0 mol L^{-1} NaHSal solution in a 500 mL four-necked flask. Subsequently, a 0.5 mol L^{-1} NaOH solution was added dropwise into the mixture under stirring until the pH reached approximately 6.7. The resulting reaction mixture was maintained at $90 \text{ }^\circ\text{C}$ for 24 h under continuous stirring. After the reaction, the solid product was collected by centrifugation, washed repeatedly with DI water, and dried at $80 \text{ }^\circ\text{C}$ for 12 h to obtain $\text{Co}_{0.1}\text{Zn-LHRs}$.

Zn-Sal LHRs, $\text{Co}_{0.05}\text{Zn-Sal}$ LHRs, $\text{Co}_{0.2}\text{Zn-Sal}$ LHRs, and Co-Sal LHRs were obtained using the same synthetic method as $\text{Co}_{0.1}\text{Zn-LHRs}$, except for the Zn: Co molar ratio (Zn: Co = 1:0, 9.5:0.5, 8:2, and 0:1, respectively).

1.3 Synthesis of Co/ZnO/C NWs

The as-prepared $\text{ZnCo}_x\text{-Sal}$ LHRs powder was carefully loaded into a porcelain boat and placed in a tube furnace, where it was annealed for 1 h at $600 \text{ }^\circ\text{C}$ with a rate of $5 \text{ }^\circ\text{C min}^{-1}$ under a 50 mL min^{-1} N_2 atmosphere. The resulting samples were denoted as ZnO/C NWs, $\text{Co}_{0.05}/\text{ZnO/C}$ NWs, $\text{Co}_{0.1}/\text{ZnO/C}$ NWs, $\text{Co}_{0.2}/\text{ZnO/C}$ NWs and Co/C NWs, respectively.

1.4 Characterization

The X-ray diffraction (XRD) patterns of the products were recorded on a Shimadzu XRD-6000 diffractometer using 40 kV, 30 mA Cu K α radiation ($\lambda = 0.154$ nm). Scanning electron microscope (SEM) observations were obtained by a Hitachi S-4700 microscope. Transmission electron microscopes (TEM) images were acquired using Hitachi H-800 and JEOL JEM-2010 microscopes. X-ray photoelectron spectroscopy (XPS) was measured by a Physical Electronic PHI Quantum 2000 system equipped with a monochromatized Al K α X-ray source. UV-visible diffused reflectance spectra (UV-vis DRS) were determined using a UV-visible spectrophotometer (UV-2600, Shimadzu).

1.5 Photoelectrochemical test

Electrochemical measurements, including electrochemical impedance spectra, Mott-Schottky analysis, and photocurrent density measurements, were performed in a three-compartment electrochemical cell using a CHI 760E electrochemical workstation with 0.1 M Na₂SO₄ as the electrolyte. Typically, 5 mg of the sample was dispersed in a mixture of 750 μ L ethanol, 200 μ L DI water, and 50 μ L 5 wt% Nafion under ultrasonic conditions for 30 min to form a homogeneous ink. The ink was then drop-cast onto cleaned fluorine-doped tin oxide (FTO) glass plates with dimensions of 1.0 \times 2.0 cm² and an effective working area of 1.0 \times 1.0 cm², which was used as the working electrode. An Ag/AgCl electrode and a Pt plate (1.0 \times 1.0 cm²) were used as the reference and counter electrodes, respectively. The light source was a 300 W xenon lamp (PLS-SXE300/300UV, 320~780 nm). The distance between the xenon lamp and the catalyst was 15 cm to ensure that the light intensity remains consistent (400 mW cm⁻²) during the test. And the voltage applied in the transient photocurrent test was the 0.5 V vs. Ag/AgCl. Besides, the transient absorption spectroscopy were tested in FLS980 (Edinburgh Instrument).

1.6 Photocatalytic performance evaluation

5 mg of as-prepared photocatalyst was dispersed in 30 mL of 50 mg L⁻¹ TC solution and stirred under dark conditions for 20 min to achieve adsorption-desorption equilibrium. Subsequently, under irradiation using a Xenon lamp as a simulated visible light source, 2.0 mL aliquots of the reaction mixture were collected at 10-minute intervals and analyzed for TC concentration using a UV-2600 spectrophotometer.

The photocatalytic degradation efficiency (η , %) of TC was calculated according to the following equation: $\eta = (1 - C_t/C_0) \times 100\%$, where C_0 denotes the initial TC concentration and C_t represents the TC concentration after degradation. The apparent photocatalytic rate constant (k) was calculated using the following equation: $k = \ln(C_0/C_t)/t$.

The band gap energy (E_g) of the sample was determined from the Kubelka-Munk equation: $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$.

1.7 The determination of reactive species

To identify the primary reactive species involved in the photocatalytic process, different radical scavengers were introduced into the photocatalytic system. Benzoquinone (BQ, 0.2 mmol L⁻¹), isopropanol (IPA, 0.2 mmol L⁻¹), and triethanolamine (TEOA, 0.2 mmol L⁻¹) were used as scavengers for superoxide radicals ($\cdot O_2^-$), hydroxyl radicals ($\cdot OH$), and photogenerated holes (h^+), respectively, in the quenching experiments.

Supporting Figures

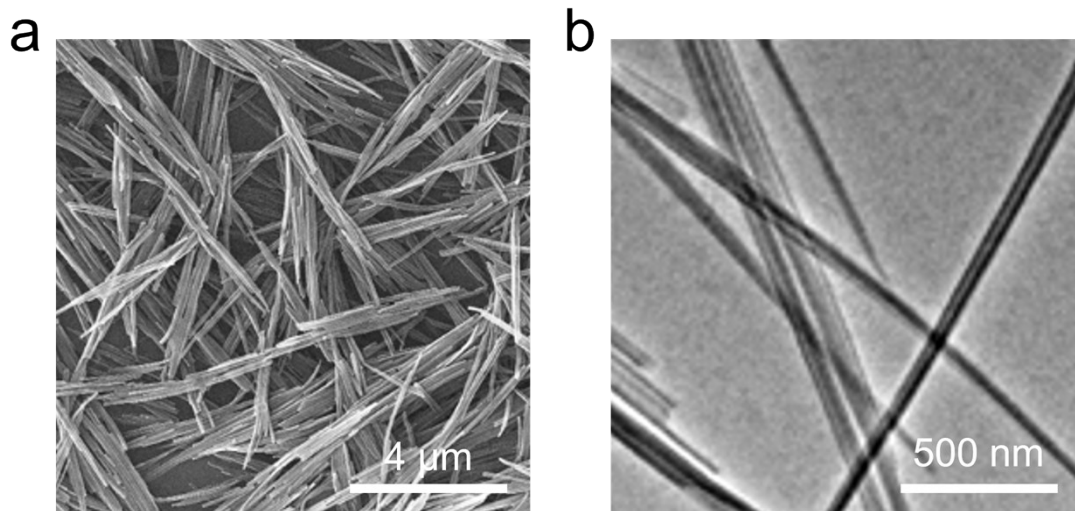


Fig. S1 (a) SEM and (b) TEM images of $\text{Co}_{0.1}/\text{ZnO}/\text{C}$ NWs.

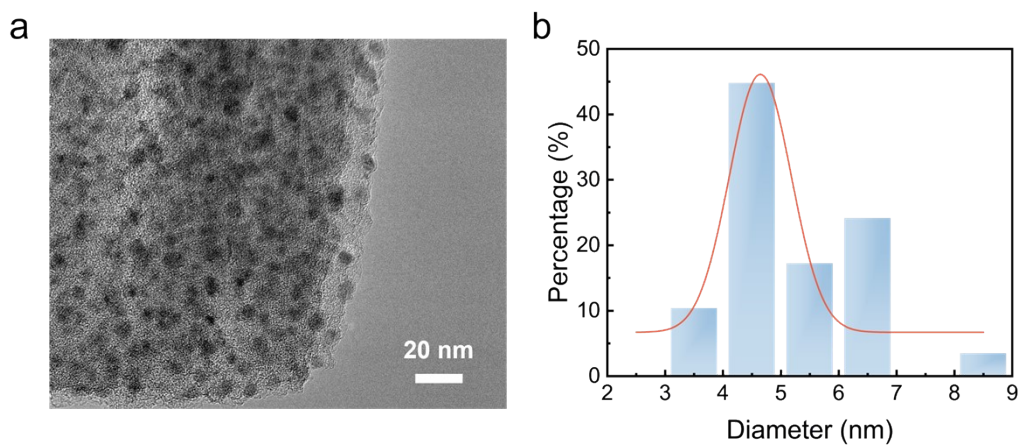


Fig. S2 (a) HRTEM image and (b) particle size statistic result of $\text{Co}_{0.1}/\text{ZnO}/\text{C}$ NWs.

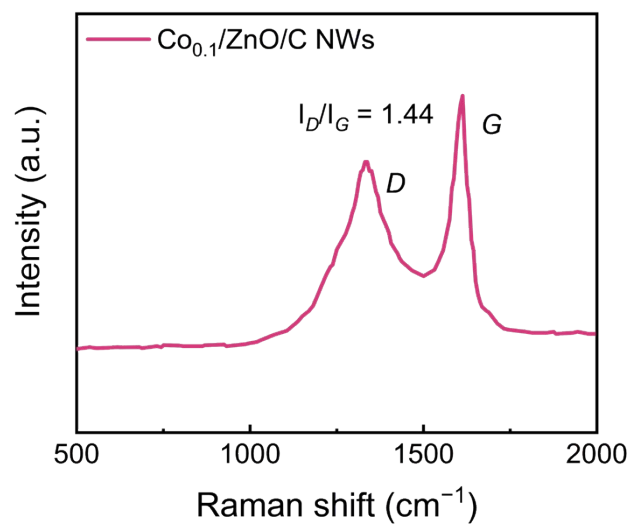


Fig. S3 Raman spectrum of Co_{0.1}/ZnO/C NWs.

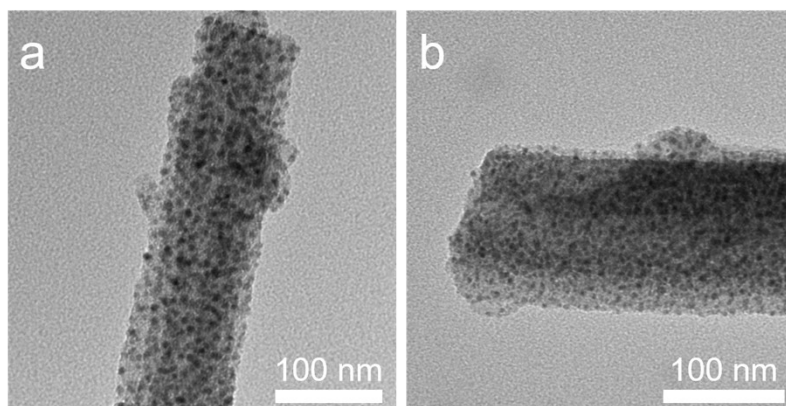


Fig. S4 TEM images of (a) Co_{0.05}/ZnO/C NWs and (b) Co_{0.2}/ZnO/C NWs.

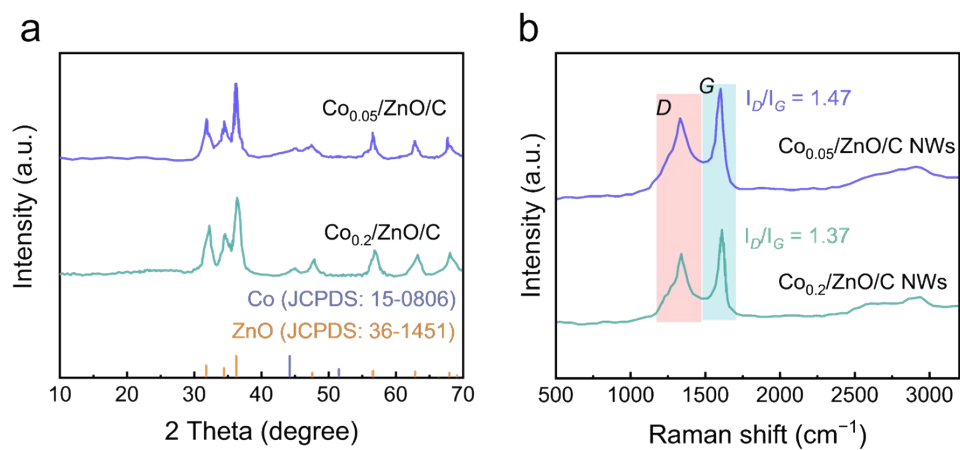


Fig. S5 XRD patterns (a) and Raman spectra (b) of $\text{Co}_{0.05}/\text{ZnO}/\text{C}$ NWs and $\text{Co}_{0.2}/\text{ZnO}/\text{C}$ NWs.

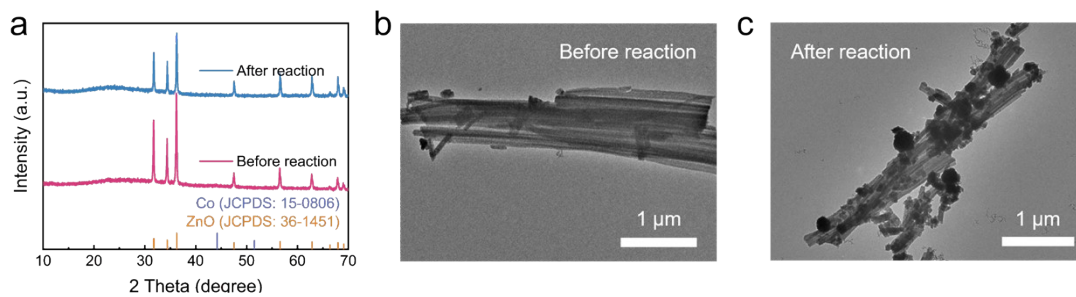


Fig. S6 (a) XRD pattern of $\text{Co}_{0.1}/\text{ZnO}/\text{C}$ NWs before and after reaction. (b, c) TEM images of $\text{Co}_{0.1}/\text{ZnO}/\text{C}$ NWs before (b) and after (c) reaction.

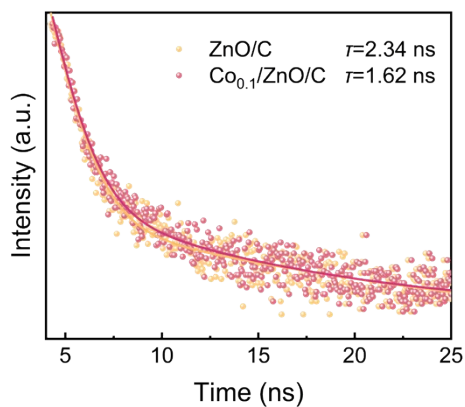


Fig. S7 The transient absorption spectroscopy results of ZnO/C NWs and Co_{0.1}/ZnO/C NWs.

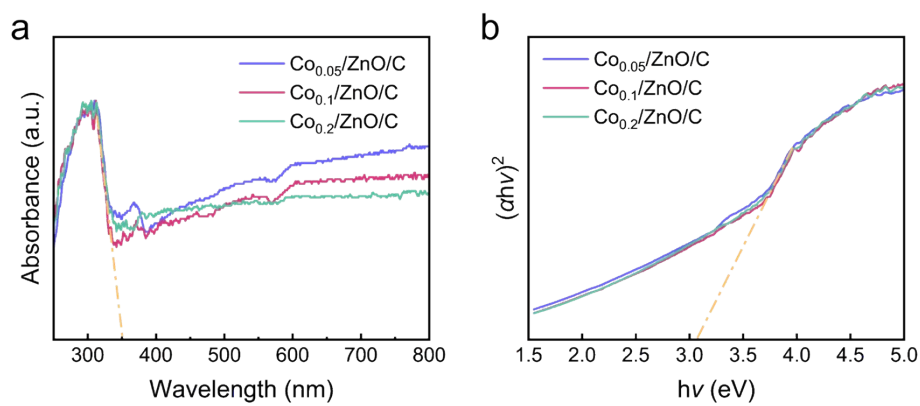


Fig. S8 (a) UV-vis DRS plots, (b) transformed Kubelka-Munk function versus photon energy of Co/ZnO/C NWs with different Co amount.

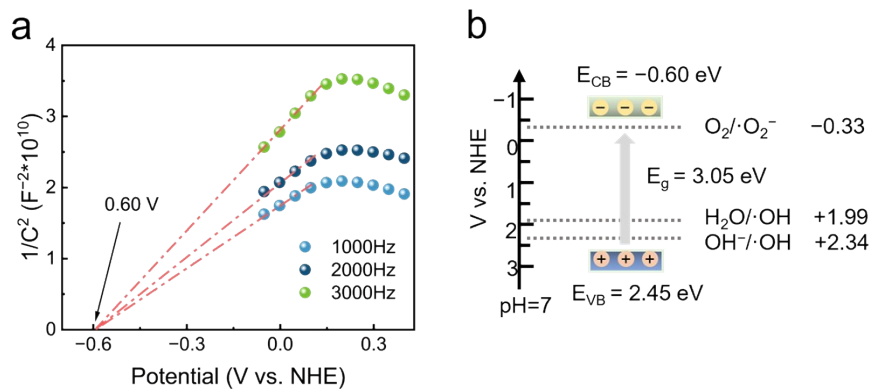


Fig. S9 (a) Mott-Schottky plot of $Co_{0.1}/ZnO/C$ NWs in 0.1 M Na_2SO_4 (pH = 7) and (b) the band structure diagram of $Co_{0.1}/ZnO/C$ NWs.

Table S1. Zn/Co ratios of the Co_{0.1}/ZnO/C NWs and corresponding precursor by inductively coupled plasma emission spectroscopy (ICP-ES).

Sample	ZnCo _{0.1} -LHRs	Co _{0.1} /ZnO/C NWs
Ratio of Zn/Co	8.97:1.03	8.85:1.15

Table S2. The binding energies of Zn 2*p* and Co 2*p*.

Sample	Zn 2 <i>p</i> Binding energy (eV)		Co 2 <i>p</i> Binding energy (eV)	
	2 <i>p</i> _{1/2}	2 <i>p</i> _{3/2}	2 <i>p</i> _{1/2}	2 <i>p</i> _{3/2}
ZnO NWs	1044.9	1021.8	—	—
Co _{0.1} /ZnO NWs	1045.2	1022.1	797.1	781.7
Co NWs	—	—	795.5	780.2

Table S3. Summary of the photocatalytic degradation of TC by different photocatalysts.

Photocatalyst	Light	Dosage	TC	Degradation rate (mg g _{cat} ⁻¹ h ⁻¹)	Ref
Ag/Bi ₂ Sn ₂ O ₇ -C ₃ N ₄	400 W Tungsten Halogen lamp	200 mg	200 mL, 20 mg L ⁻¹	1.49	1
BIM-34	300 W-Xe lamp	20 mg	100 mL, 10 mg L ⁻¹	45.80	2
CWB-2	300 W-Xe lamp	20 mg	50 mL, 20 mg L ⁻¹	48.65	3
MIL-101(Fe)/CN/FOC-0.5	300 W-Xe lamp	20 mg	100 mL, 20 mg L ⁻¹	97.40	4
BiOI/BiOIO ₃	500 W-Xe lamp	50 mg	50 mL, 20 mg L ⁻¹	3.37	5
Co _{0.1} /ZnO/C NWs	300 W-Xe lamp	10 mg	30 mL, 50 mg L ⁻¹	147.96	This work

Table S4 Catalyst mass recovered via magnetic separation after five consecutive cycles.

Cycle	0	1	2	3	4	5
Mass (mg)	10.00	9.92	9.71	9.63	9.61	9.54

Table S5 The kinetic analysis of emission decay for Co/ZnO/C NWs.

Sample	τ_1	τ_2	τ_{average}
ZnO/C	1.22	17.18	2.34
Co _{0.1} /ZnO/C	1.18	10.02	1.62

References

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