



# Insights into Photocatalytic Degradation Pathways and Mechanism of Tetracycline by an Efficient Z-Scheme NiFe-LDH/CTF-1 Heterojunction

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## 1. Methods

### 1.1. Material and Electrochemical Characterization

Powder X-ray diffraction (PXRD) patterns were obtained on a Bruker D8-advance (Billerica, MA, USA) diffractometer equipped with Cu K $\alpha$  radiation, operating at a  $2\theta$  range from 5° to 80°. Fourier transform infrared (FT-IR) spectra were recorded in the range 4000 to 600 cm<sup>-1</sup> by using KBr pellets on a Thermo Scientific Nicolet iS10 spectrometer (Boston, MA, USA). X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum 2000 XPS (Washington, WA, USA) system equipped with a monochromatic Al K $\alpha$  X-ray source. The C 1s peak (284.6 eV) of the surface adventitious carbon was used as the internal reference. Ultra-high resolution scanning electron microscopy (HRSEM) images and Transmission electron microscopy (TEM) images were collected using a Verios G4 UC microscopy (FEI Corp., Hillsboro, OR, USA) and a Tecnai G2 F20 microscope (FEI Corp., Hillsboro, OR, USA), respectively. Nitrogen adsorption and desorption isotherms were carried out at 77 K on an ASAP 2020 apparatus (Micromeritics Instrument Corp., Norcross, GE, USA) and the Brunauer-Emmett-Teller (BET) method was used to calculate the surface area. UV-vis diffuse reflectance spectra (UV-vis DRS) were measured with a Varian Cary 500 UV-vis spectrophotometer (Palo Alto, CA, USA) by using the powder samples with BaSO<sub>4</sub> as the reflectance standard. The photoluminescence (PL) spectra were recorded using an Edinburgh FL/FS 900 (Edinburgh, United Kingdom) spectrophotometer with 330 nm excitation light. The electron spin response (ESR) signals of free radicals were examined on a spectrometer (Bruker A300, Billerica, MA, USA) under visible light irradiation ( $\lambda > 420$  nm) using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin-trapped reagent.

The electrochemical properties of the catalysts were determined in a cell with three electrodes on a CHI650E electrochemical workstation. The as-prepared sample, a platinum sheet and Ag/AgCl were applied as the working, reference and counter electrodes, respectively. We fabricated the working electrode through the following process: a 5 mg photocatalyst was immersed in 0.5 mL N, N-dimethylformamide (DMF) and sonicated for 30 min, and then the 10  $\mu$ L suspension was coated onto fluoride-tin oxide (FTO) glass with a size of 0.5 cm  $\times$  0.5 cm. The other area of the FTO glass was smeared with epoxy resin to keep insulated, and then the electrode was dried overnight. The Mott-Schottky and electrochemical impedance spectroscopy (EIS) plots were evaluated through a ZAHNER IM6 in a mixed aqueous solution of KCl (0.1 M), Na<sub>2</sub>SO<sub>4</sub> (0.2 M), K<sub>3</sub>[Fe(CN)<sub>6</sub>] (5 mM) and K<sub>4</sub>[Fe(CN)<sub>6</sub>] (5 mM). The photocurrent data were recorded on the CHI650E

electrochemical workstation, where the electrolyte and a light source were 0.2 M Na<sub>2</sub>SO<sub>4</sub> and a 300 W Xe lamp equipped with a 420 nm filter, respectively.

### 1.2. Identification of the Degradation Intermediates

The degradation intermediates of TC were identified by a TSQ Quantum Access MAX LC-MS system (Boston, MA, USA) equipped with an Agilent ZORBAX Eclipse Plus C18 (Palo Alto, CA, USA) column (250 × 4.6 mm, 5 μm). The isocratic mobile phase was 0.1% (v/v) of formic acid aqueous solution and acetonitrile (70:30) at a flow rate of 0.8 mL min<sup>-1</sup>. The injection volume was 10 μL, and the column temperature was 30 °C. UV absorption, at a wavelength of 360 nm, was used for detection. And eluted compounds were detected between m/z 50 and 600.

## 2. Supplementary Figures

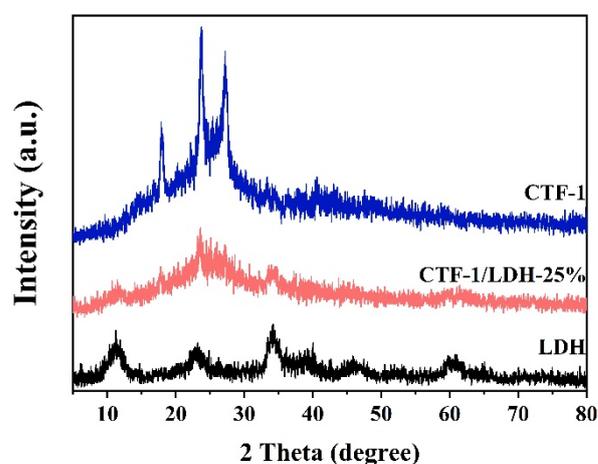


Figure S1. XRD patterns of pure LDH, CTF-1, and the CTF-1/LDH-25%.

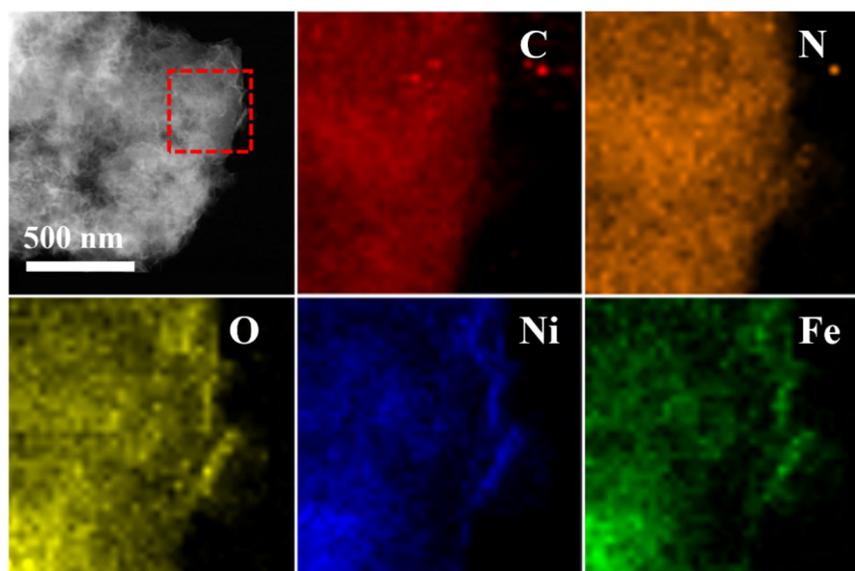


Figure S2. EDX elemental mapping images of the LDH/CTF-1-40% nanocomposite.

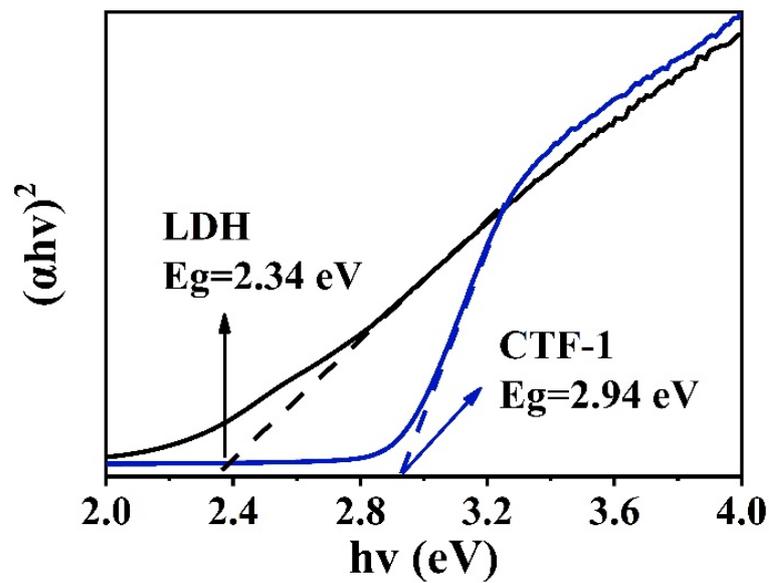


Figure S3. Plots of  $(\alpha hv)^2$  vs. the energy of absorbed light for pure LDH, CTF-1 and the LDH/CTF-1 nanocomposites.

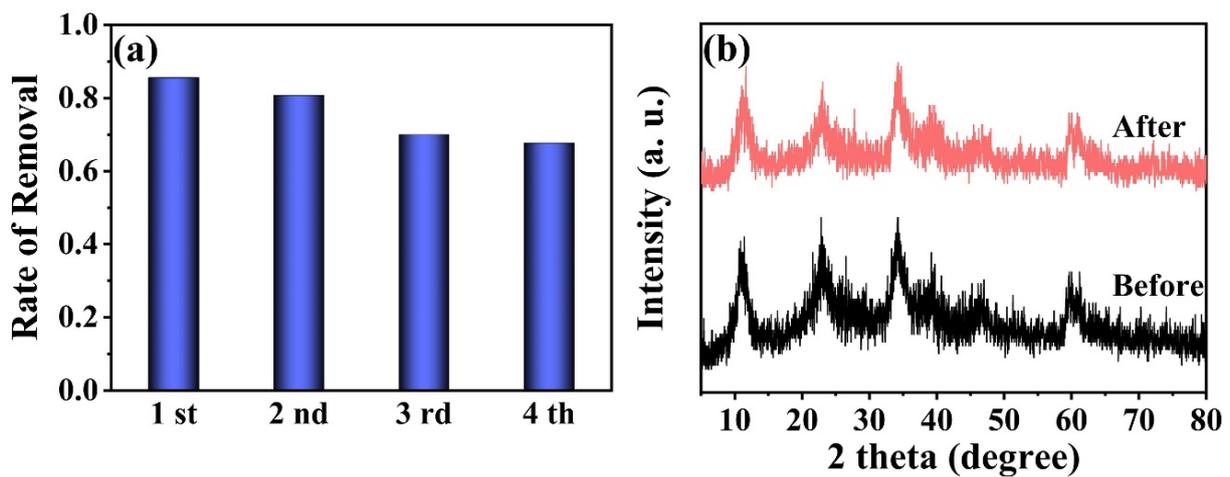


Figure S4. Cycling runs for degradation efficiency of TC (a) and XRD patterns of before and after reaction (b) over the LDH/CTF-1-40%.

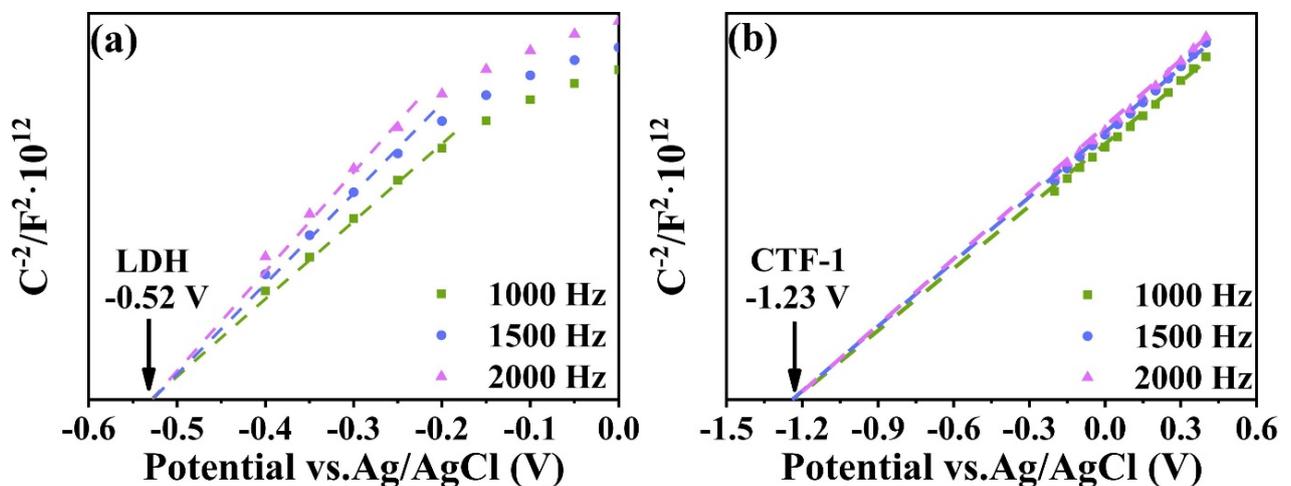


Figure S5. Mott-Schottky of LDH (a) and CTF-1 (b).

**Table S1.** Toxicity prediction of TC and its intermediates.

Toxic endpoint	Fathead minnow LC <sub>50-96 h</sub> (mg L <sup>-1</sup> )	Oral rat LD <sub>50</sub> (mg L <sup>-1</sup> )	Mutagenicity
TC	0.90	1068.64	0.60 (positive)
P1	0.79 (-)	1615.37 (+)	0.64 (positive)
P2	0.47 (-)	1568.39 (+)	0.65 (positive)
P3	2.75 (+)	1317.21 (+)	0.81 (positive)
P4	603.22 (+)	1656.29 (+)	0.23 (negative)
P5	0.85 (+)	1029.30 (-)	0.65 (positive)
P6	3.36 (+)	NA	0.91 (positive)
P7	90.24 (+)	3679.6 (+)	0.13 (negative)
P8	3.74 (+)	NA	-0.03 (negative)