

Supporting Information

Enhanced Removal of Veterinary Antibiotic Florfenicol by Cu-based Fenton-like Catalyst with Wide pH Adaptability and High Efficiency

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Text S1

Reusability. To investigate the stability and reusability of the screened CuNiFeLa-2-LDH, the catalyst was filtered after each reaction and washed with ultrapure water more than 3 times until the pH of the supernatant reached 7.0. Then, the filtered powder was dried at 40 °C. The regenerated materials were used for five cycles to degrade the solution of 10 mg·L⁻¹ FF. During each cycle, the degradation efficiency was calculated by detecting the concentration of residual FF.

Text S2

ROS trapping. For identifying the role of the reactive oxygen species (ROS) during the reaction process, tert-Butanol (TBA), p-benzoquinon (BQ), sodium azide (NaN₃) were used as the scavengers of hydroxyl radicals ($\bullet\text{OH}$), superoxide radical ($\bullet\text{O}_2^-$) and singlet oxygen (O_2^1). The signal of hydroxyl radicals was detected by photoluminescence (PL) emission spectra using a benzoic acid method at room temperature with the excitation wavelength at 316 nm.¹ Briefly, a certain amount of catalyst was mixed with 50 mL of benzoic acid (10 mmol·L⁻¹), FF (10 mg·L⁻¹) and H₂O₂ (5 mmol · L⁻¹) solution. After the beginning of the reaction, a certain amount of supernatant was taken from the reactor at a designed time intervals, and then the filtered solution was analyzed by PL emission spectroscopy to indirectly measure the amount of hydroxyl radicals.

Text S3

ESR measurement. In addition, the electron spin resonance (ESR) spectra with DMPO ($\cdot\text{OH}$, $\cdot\text{O}_2^-$) and TEMP ($\text{O}_2^{\cdot 1}$) as trapping reagents was used to detect the ROS on a Miniscope MS-5000 ESR spectrometer (microwave frequency: 9.47 GHz; microwave power: 10 mW; modulation: 0.2 mT; and sweep time: 60 s). The signal of $\cdot\text{OH}$, $\cdot\text{O}_2^-$ and $\text{O}_2^{\cdot 1}$ with and without catalyst or H_2O_2 were detected in the aqueous solution and DMSO solution, respectively. In a typical procedure, the ESR measurement of each sample was prepared by adding 5 mg catalyst to 2 mL water or DMSO. Then, 1 mL of the above suspension, 5 μL DMPO and 10 μL H_2O_2 (30%, w/w) were mixed. After 5 min, the ESR spectra was recorded on the ESR spectrometer.

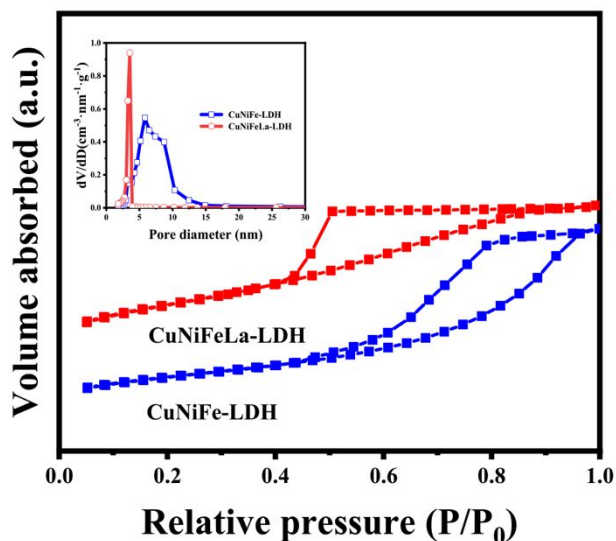


Figure S1. N_2 adsorption-desorption isotherms for CuNiFe-LDH, CuNiFeLa-2-LDH (the inset represents pore size distribution calculated from the desorption branch data by the BJH method).

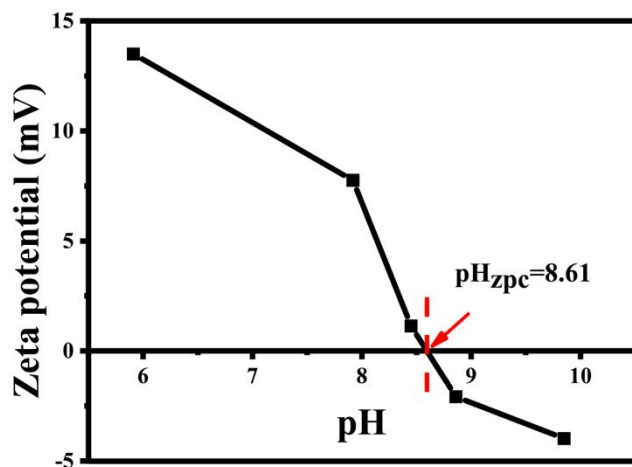


Figure S2. Zeta potential of CuNiFeLa-2-LDH

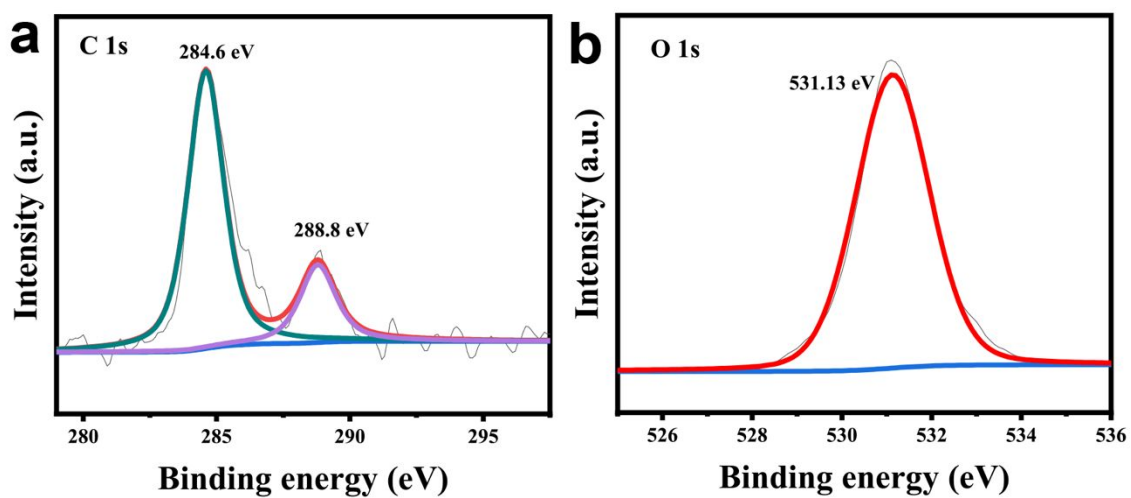


Figure S3. The high resolution XPS spectrum of CuNiFeLa-2-LDH (a) C 1s and (b) O 1s.

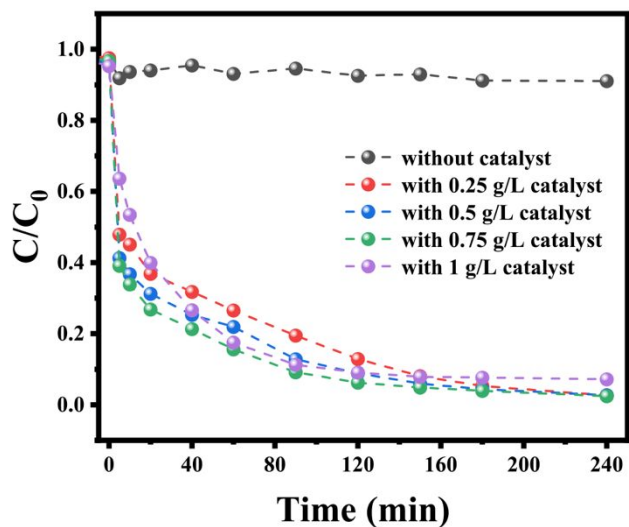


Figure S4. Effects of catalyst dosage on degradation of FF by CuNiFeLa-2-LDH. Conditions:

$[\text{H}_2\text{O}_2]=5 \text{ mmol}\cdot\text{L}^{-1}$, $[\text{FF}]=10 \text{ mg L}^{-1}$, natural pH.

Table S1. Chemical composition analysis of La-doped CuNiFe-LDHs

Materials	$m(\text{Cu})$ a%	$m(\text{Ni})$ a%	$m(\text{Fe})$ a%	$m(\text{La})$ a%	$M(\text{Cu}/\text{Ni}/\text{Fe}/\text{La})^b$	Chemical composition
CuNiFeLa-1-LDH	6.83	18.68	11.14	1.38	1:2.96:1.85:0.09	$[\text{Cu}^{2+}_{0.17}\text{Ni}^{2+}_{0.50}\text{Fe}^{3+}_{0.31}\text{La}^{3+}_{0.02}(\text{OH})_2]^{0.33+}(\text{CO}_3^{2-})_{0.165}\cdot\text{mH}_2\text{O}$
CuNiFeLa-2-LDH	6.99	19.00	10.34	2.41	1:2.94:1.68:0.16	$[\text{Cu}^{2+}_{0.17}\text{Ni}^{2+}_{0.51}\text{Fe}^{3+}_{0.29}\text{La}^{3+}_{0.03}(\text{OH})_2]^{0.32+}(\text{CO}_3^{2-})_{0.16}\cdot\text{mH}_2\text{O}$
CuNiFeLa-3-LDH	6.16	16.64	8.08	4.08	1:2.93:1.49:0.30	$[\text{Cu}^{2+}_{0.17}\text{Ni}^{2+}_{0.51}\text{Fe}^{3+}_{0.26}\text{La}^{3+}_{0.06}(\text{OH})_2]^{0.32+}(\text{CO}_3^{2-})_{0.16}\cdot\text{mH}_2\text{O}$
CuNiFeLa-4-LDH	5.93	15.85	6.00	14.09	1:2.89:1.15:1.09	$[\text{Cu}^{2+}_{0.16}\text{Ni}^{2+}_{0.47}\text{Fe}^{3+}_{0.19}\text{La}^{3+}_{0.18}(\text{OH})_2]^{0.37+}(\text{CO}_3^{2-})_{0.185}\cdot\text{mH}_2\text{O}$

^a Mass content of Cu, Ni, Fe or La in the material.

^b Cu/Ni/Fe/La molar ratio.

Table S2. EDS results of element analysis

El	AN	Series	Unn. C wt. %	Norm. C wt. %	Atom. C at. %	Error wt. %
O	8	K-series	35.65	38.23	55.29	4.5
C	6	K-series	12.89	13.83	26.64	2.4
Ni	28	K-series	21.46	23.01	9.08	0.6
Fe	26	K-series	11.14	11.95	4.95	0.3
Cu	29	K-series	8.84	9.48	3.45	0.3
La	57	L-series	3.27	3.51	0.58	0.1
Total:			93.26	100.00	100.00	

REFERENCES

(1) Zhou, L.; Lei, J. Y.; Wang, L. Z.; Liu, Y. D.; Zhang, J. L., Highly efficient photo-Fenton degradation of methyl orange facilitated by slow light effect and hierarchical porous structure of Fe₂O₃-SiO₂ photonic crystals. *Appl. Catal. B: Environ.* **2018**, 237, 1160-1167.