Supplementary Materials

Cu_2O-CuX NPs rich in oxygen vacancies modulated by halogen ions and its applications in photocatalytic degradation

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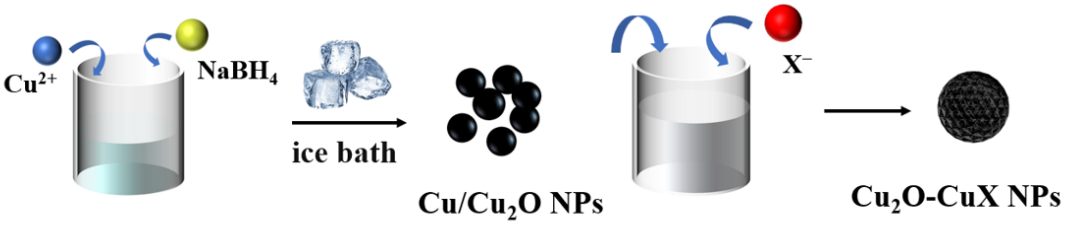
Chemicals, Reagents

Methylene blue (MB) and glutathione (GSH) were purchased from Aladdin Industrial Co., Ltd. (Shanghai, China). Copper chloride ($CuCl_2 \cdot 2H_2O$) was bought from Macklin Biochemical Co., Ltd. (Shanghai, China). Ammonium hydrogen fluoride (NH_4HF_2) was bought from Shengao Chemical Reagents Co., Ltd. (Tianjin, China). Sodium chloride (NaCl) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Potassium iodide (KI) and potassium bromide (KBr) were bought from Macklin Biochemical Co., Ltd. (Shanghai, China). Sodium borohydride ($NaBH_4$) was obtained from Tianjin Yongda Chemical Reagent Co., Ltd. All reagents were analytical grade and were used without further purification. The aqueous solutions were prepared using ultrapure water (18.25 MΩ cm).

Apparatus

The UV xenon lamp for photocatalytic experiments was purchased from Beijing Porphyry Science and Technology Company with the model number PLX-SXE300+/UV. The PEC system consists of a CHI660E electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China) and a PEAC 200A PEC reaction instrument (Tianjin Aidahengsheng Science-Technology Development Co., Ltd., China). PEC experiments were conducted on the PEC system using a three-electrode system: an ITO electrode with a geometric area of 0.25 cm^2 as the working electrode, a saturated Ag/AgCl electrode as the reference electrode, and a Pt wire as the counter electrode. The electron paramagnetic resonance (EPR) spectra measurement was recorded by using a JES FA200 spectrometer (JEOL, Japan) at room temperature. X-ray powder diffraction (XRD) patterns were obtained with a Rigaku-Mini Flex 600 (Tokyo, Japan). Scanning electron microscopy (SEM) and transmission electron microscope (TEM) images were obtained on a Hitachi S-4800 (Tokyo, Japan) and a Tecnai G2 F20 TEM (FEI Co., Hillsboro, Oregon, USA), respectively. UV-visible diffuse reflection spectra were recorded using a PerkinElmer Lambda 950 UV-visible spectrophotometer (United States). X-ray photoelectron spectroscopy (XPS) images were recorded on a K-Alpha X-ray photoelectron spectrometer (Thermo Fisher Scientific Co., Waltham, MA, United States).



Scheme S1. The preparation steps of the materials.

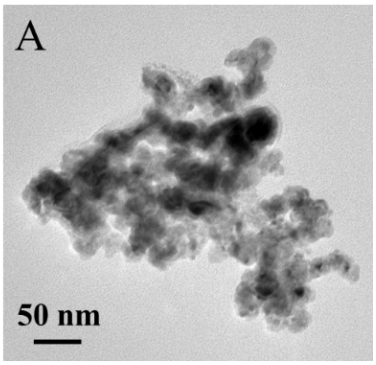


Fig. S1 TEM images of Cu/Cu_2O NPs.

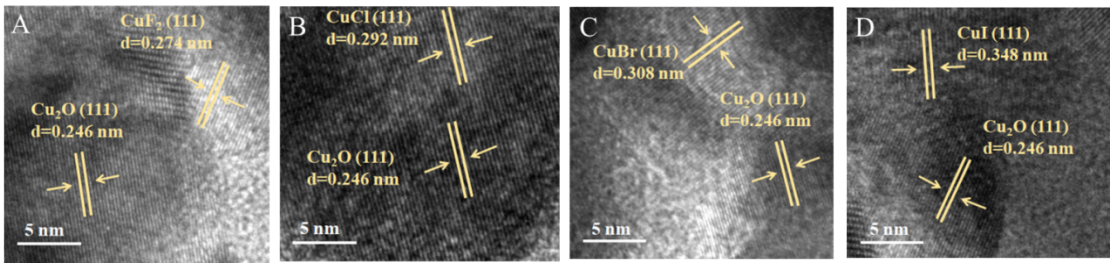


Fig. S2 HRTEM images of (A) Cu_2O-CuF_2 NPs, (B) Cu_2O-CuCl NPs, (C) Cu_2O-CuBr NPs, and (D) Cu_2O-CuI NPs.

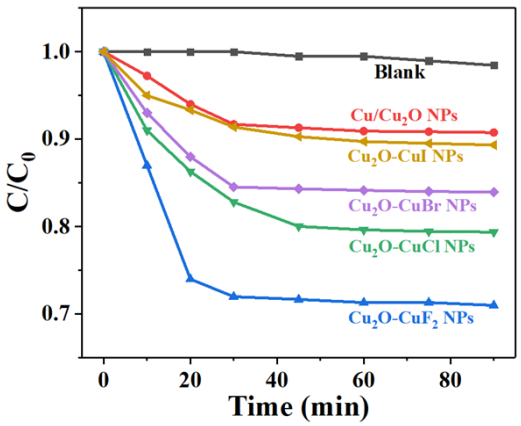


Fig. S3 Adsorption-desorption curves of different photocatalysts over 90 minutes.

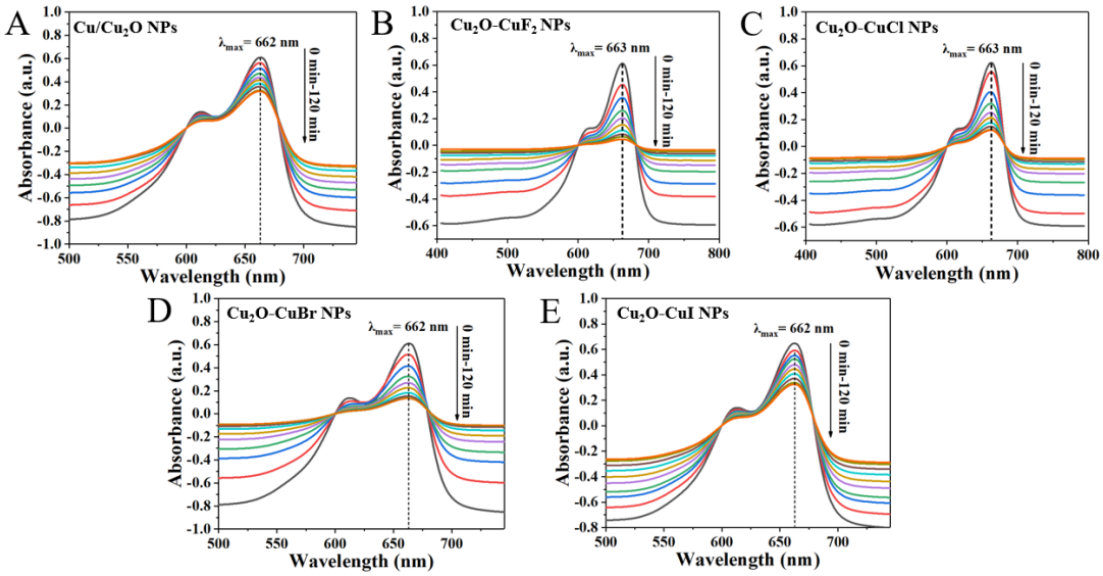


Fig. S4 UV-Vis test of (A) Cu/Cu_2O NPs, (B) Cu_2O-CuF_2 NPs, (C) Cu_2O-CuCl NPs, (D) Cu_2O-CuBr NPs, and (E) Cu_2O-CuI NPs.

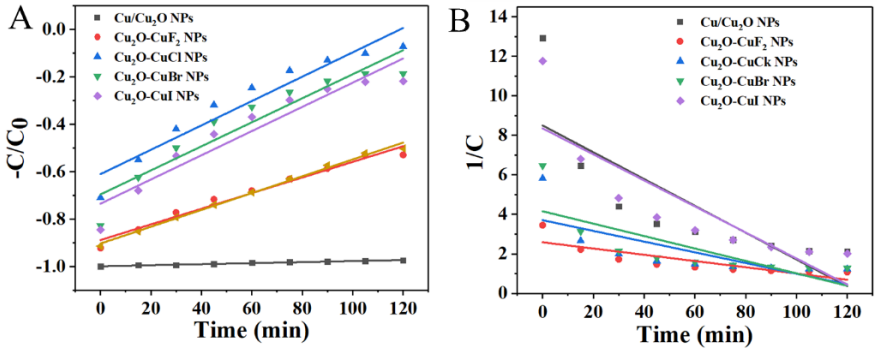


Fig. S5 Photocatalytic degradation fits (A) the zero-order (B) the second-order kinetic equation curve.

Table S1. Different Cu_2O-CuF_2 NPs catalytic fitting kinetic parameters

Kinetic Model	Equation	R^2	Rate Constant (k)
Zero-order	$C_0 - C = k_0 \cdot t$	0.916	0.0051 mol L^{-1} min^{-1}
First-order	**$\ln(C_0/C) = k_1 \cdot t$**	**0.986**	**0.0052 min^{-1}**
Second-order	$1/C - 1/C_0 = k_2 \cdot t$	0.8881	0.096 $L \cdot mg^{-1} \cdot min^{-1}$

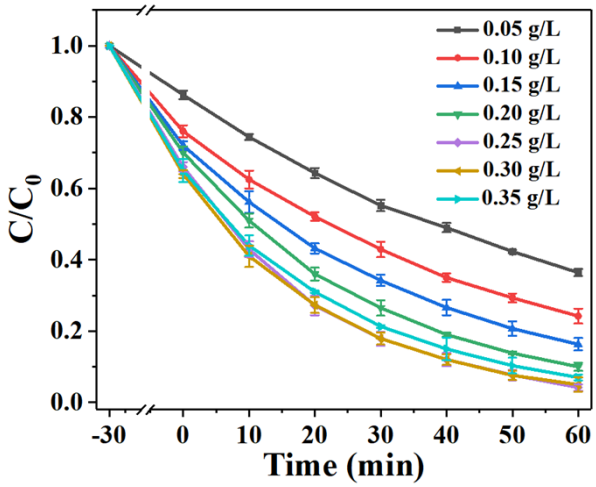


Fig. S6 Influence of Cu_2O-CuF_2 NPs dose.

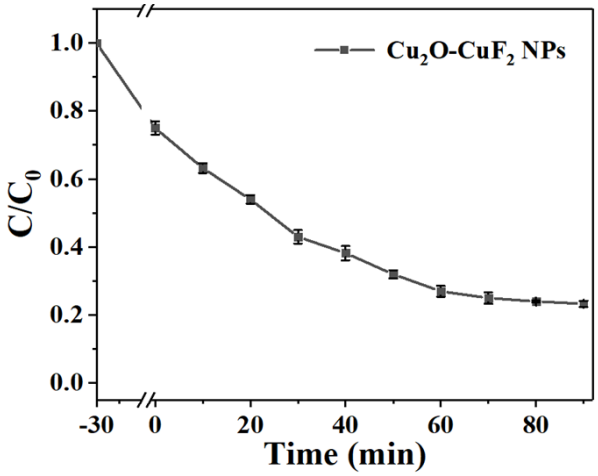


Fig. S7 Photocatalytic degradation of RhB by Cu_2O-CuF_2 photocatalysis;

Table S2. Comparison of this photocatalyst with other photocatalysts

Catalyst	Model dye	Source of light energy	Illumination time	Degradation efficiency(%)	References
Al substituted ZnO nanoparticles	MB	UV-light	120 min	99.7	[1]
Zn-TiO_2-LDO-6	MB	UV-light	180 min	98.3	[2]
Fe/ZnO	MB	UV-light	100 min	96.7	[3]
Ag_2S	MB	UV-light	100 min	93.4	[4]
Cu_1−ZnO/GPET	MB	UV-light	420 min	83.6	[5]
Cu_2O-CuF_2	MB	UV-light	60 min	95.8	This work

References

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