Supplementary Information (SI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2025

Supporting Information

Constructing Zero-Valent Nanotwinned Copper for the Ignition of [BMIM]N(CN)₂-H₂O₂ Green Propellant

Qing Cheng^{a, b}, Yuqi Zhang^{a, b}, Yingying Cao^a, Peihao Dou^b, Long Liu^{*c}, Yanqiang Zhang^{*b, c}

- ^a College of Chemistry and Molecular Sciences, Henan University, Zhengzhou 450046, China. E-mail: yqzhang@ipe.ac.cn.
- ^b Zhengzhou Institute of Emerging Industrial Technology, Longzihu New Energy Laboratory, Zhengzhou 450000, China.

^c Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China.

CONTENTS

Theoretica	l calculations1
XRD refine	e ment 1
EPR spectr	a quantification2
Ignition ex	periment operation2
Figure S1.	Color change process of the solution during the synthesis of <i>T</i> -Cu2
Figure S2.	(a) SEM image of T-Cu. (b) Particle size distribution of T-Cu. (c) and (d)
	SEM image and elemental distribution maps of <i>T</i> -Cu
Figure S3.	(a) HRTEM image of T-Cu. (b) Corresponding inverse FFT image taken
	from the white dashed square in (a). (c) HRTEM image of T-Cu. (d)
	Crystal lattice distance of T-Cu. (e) Atomic-resolution HRTEM and
	scheme of T-Cu, corresponding to the enlarged orange dashed square area
	in (c)
Figure S4.	SEM image and particle size distribution of T-Cu synthesized at 10x
	magnification4
Figure S5.	(a) HRTEM image of C-Cu. (b) Corresponding inverse FFT image. (c)
	Crystal lattice distance of C-Cu4
Figure S6.	XPS surevy spectra of T-Cu, C-Cu and immersed in BMIM][N(CN) ₂ IL
	for two weeks5
Figure S7.	Comparison of catalytic performance under similar dosages of catalysts
	for spontaneous ignition of N(CN)2 ⁻ -based IL-H2O2 system ⁸⁻¹⁰ 5
Figure S8.	In situ FT-IR spectra of the C-Cu catalyzed H ₂ O ₂ process6
Figure S9.	(a) Slab model of Cu (111) crystal plane. (b) Slab model of Cu (111) after
	horizontal flipping. (c) Twinned Cu (111) model after splicing. (d) Twin
	Cu (111) model after structure optimization
Figure S10	. C-Cu (111) model (a) before and (b) after structural optimization
Figure S11	. Charge density difference distribution of C-Cu (a and b) and T-Cu (c and
	d) in different directions7
Reference	7

Theoretical calculations

All the energies of geometrical configuration were obtained within density functional theory (DFT) calculation using the Vienna *ab initio* Simulation Package (VASP ver. 6.3.2) ¹⁻³. The projector augmented wave (PAW) method was used to describe the electron-ion interactions with the cutoff energy of up to 400 eV⁴. The exchange and correlation energies were described by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional⁵. The Brillouin zone sampling was performed on gamma point only⁶. The geometrical configurations were relaxed until the forces acting on atoms were smaller than $0.02 \text{ eV} \cdot \text{Å}^{-1}$ or the change of total energy in each step was smaller than $1 \times 10^{-4} \text{ eV}$. The 4-layer Cu (111) slab models were used to build the calculation model, and an additional vacuum layer of 15 Å was added to the model to avoid the artificial interaction effect between the slab and their mirror images. The geometrical configurations and charge density difference distribution were illustrated with VESTA software⁷.

XRD refinement

The powder X-ray diffraction data were refined using the Rietveld method in Rigaku PDXL 2.4 software. A Cu K α radiation source ($\lambda = 1.5406$ Å) with a D/teX detector was employed. The pseudo-Voigt function was selected to model peak profiles, and instrumental broadening was corrected via Caglioti parameters ($U = 0.018^{\circ 2}$, $V = -0.002^{\circ}$, $W = 0.006^{\circ}$). A 6th-order polynomial was used for background subtraction. Structural parameters, including lattice constants (a = 5.430(1) Å, space group *Pnma*) and atomic coordinates (e.g., Fe1 at Wyckoff 4a site), were refined sequentially. Site occupancies were constrained to match XRF-derived stoichiometry. The final agreement indices ($R_{wp} = 7.2$ %, $\chi^2 = 1.9$) and the visual fit (observed vs. calculated patterns) confirmed the model reliability.

EPR spectra quantification

A 50 μ L mixed solution (consisting of 5 μ L of 1 mg/mL T-Cu/C-Cu+[BMIM]N(CN)₂ mixture, 5 μ L of 30% H₂O₂ oxidizer, 5 μ L of 100 mM PBN spin trap, and 35 μ L water) was loaded into a quartz capillary with an inner diameter of 0.9 mm, and the bottom end was sealed with wax. The capillary was then inserted into the EPR cavity for spectral acquisition. The test parameters were set as follows: 20 dB microwave attenuation, 20 mW microwave power, magnetic field range of 3460–3560 G, microwave frequency of 9.85 GHz, and magnetic field modulation amplitude of 1 G.

Ignition experiment operation

First, 10 wt% *T*-Cu/*C*-Cu catalysts were mixed with 90 wt% [BMIM]N(CN)₂ ionic liquid (IL). The resulting mixtures were sonicated at 25 °C and 300 W for 30 minutes. A 15 mL cylindrical open-mouth glass vial containing 1.5 mL of 98% H₂O₂ served as the oxidizer pool. A droplet of the mixtures of 10 wt% *T*-Cu/*C*-Cu + 90 wt% [BMIM]N(CN)₂ were dropped into the oxidizer pool. The ignition process was recorded using a high-speed camera at 5000 frames·s⁻¹, and the reported data represent the average of three independent ignition tests.



Figure S1. Color change process of the solution during the synthesis of *T*-Cu.



Figure S2. (a) SEM image of *T*-Cu. (b) Particle size distribution of *T*-Cu. (c) and (d) SEM image and elemental distribution maps of *T*-Cu.



Figure S3. (a) HRTEM image of *T*-Cu. (b) Corresponding inverse FFT image taken from the white dashed square in (a). (c) HRTEM image of *T*-Cu. (d) Crystal lattice distance of *T*-Cu. (e) Atomic-resolution HRTEM and scheme of *T*-Cu, corresponding to the enlarged orange dashed square area in (c).



Figure S4. SEM image and particle size distribution of *T*-Cu synthesized at 10x magnification



Figure S5. (a) HRTEM image of *C*-Cu. (b) Corresponding inverse FFT image. (c) Crystal lattice distance of *C*-Cu.



Figure S6. XPS surevy spectra of *T*-Cu, *C*-Cu and immersed in BMIM][N(CN)₂ IL for two weeks.



Figure S7. Comparison of catalytic performance under similar dosages of catalysts for spontaneous ignition of N(CN)₂⁻-based IL-H₂O₂ system⁸⁻¹⁰.



Figure S8. In situ FT-IR spectra of the C-Cu catalyzed H₂O₂ process.



Figure S9. (a) Slab model of Cu (111) crystal plane. (b) Slab model of Cu (111) after horizontal flipping. (c) Twinned Cu (111) model after splicing. (d) Twin Cu (111) model after structure optimization.



Figure S10. C-Cu (111) model (a) before and (b) after structural optimization.



Figure S11. Charge density difference distribution of *C*-Cu (a and b) and *T*-Cu (c and d) in different directions.

Reference

- [1] G. Kresse, D. Joubert, Phys. Rev. B, 1999, 59, 1758.
- [2] G. Kresse, J. Furthmüller, Phys. Rev. B, 1996, 54, 11169.
- [3] G. Kresse, J. Furthmüller, Comput. Mater. Sci., 1996, 6, 15.
- [4] P. E. Blöchl, Phys. Rev. B, 1994, 50, 17953.
- [5] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865.
- [6] H. J. Monkhorst, J. D. Pack, Phys. Rev. B, 1976, 13, 5188.
- [7] K. Momma, F. J. Izumi. Appl. Crystallogr., 2011, 44, 1272.
- [8] K. Wang, T. Liu, Y. Jin, S. Huang, N. Petrutik, D. Shem Tov, Q. L. Yan, M. Gozin, Q. Zhang, J. Mater. Chem. A, 2020, 8, 14661-14670.
- [9] S. C. Liao, T. L. Liu, Z. Y. Zhou, K. C. Wang, and Q. H. Zhang, *Energ. Mater. Front.*, 2024, 5, 41-46.
- [10]Q. Cheng, Y. Yao, P. Dou, L. Liu, Y. Cao, Y. Zhang, J. Mater. Chem. A, 2024, 12, 21425-21433.