

SUPPORTING INFORMATION

Improved Charge Carrier Mobility in a Copper Oxide Heterostructure Enhances the Photocatalytic Partial Oxidation of Benzyl Alcohol to Benzaldehyde

Chemicals

CuSO₄ (≥99%, Sigma-Aldrich), sodium dodecyl sulphate (≥99%, Sigma-Aldrich), ascorbic acid (≥99%, Sigma-Aldrich), NH₄OH (28%, ≥99.99%, Sigma-Aldrich), NaOH (ChemPure), benzyl alcohol (99.5%, ChemPure), benzaldehyde (≥99.5%, ChemPure), acetonitrile (HPLC grade, POCH™), KI (≥99.5%, ChemPure), 5,5-dimethyl-1-pyrroline N-oxide, DMPO (≥99%, Sigma-Aldrich), 2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPO (99%, Sigma-Aldrich), 2,2,6,6-Tetramethylpiperidine, TEMP (≥99%, Sigma-Aldrich), sodium azide, NaN₃ (≥99.5%, Sigma-Aldrich), 1,4-benzoquinone (≥98%, Sigma-Aldrich), AgNO₃ (99.8%, Stanlab), *tert*-Butanol (≥99%, Carl Roth), terephthalic acid (98%, Sigma-Aldrich), Cu₂O (≥99.99%, Sigma Aldrich), Cu₂O (99.5%, FUJIFILM Wako), and CuO (99.9%, FUJIFILM Wako) were used as received without any further purification. Milli-Q water was used throughout all the experiments.

Characterization

The microstructure was checked with X-ray powder diffraction (XRD, Siemens D5000). The morphology was examined with scanning electron microscopy (SEM, JSM-7610F Jeol) and transmission electron microscopy (TEM, JEM-2100 Jeol). An adsorption instrument (Belsorp 28SA Bel) was used to examine the textural properties. The diffuse reflectance (DR) spectra were recorded with a UV-Vis-NIR spectrophotometer (Lambda 950, Perkin Elmer) to characterize the optical properties. Time-resolved microwave conductivity (TRMC) measurements were performed with the third harmonic (460 nm) of a Nd:YAG laser (Vibrant II, Oportek) for visible excitation. Light-induced infrared (IR) absorption spectra were obtained with a Fourier transform spectrometer (FT/IR610, Jasco). The time-resolved fluorescence (TRFL) spectra were recorded by spectrophotometer (HORIBA Jobin Yvon, Fluorolog-3) with an excitation wavelength of 440 nm. X-ray photoelectron spectra (XPS) was recorded on ULVAC-PHI (PHI X-tool). X-ray absorption spectroscopy (XAS) was performed at Siam Photon Laboratory, while the XAS data processing was done with Demeter software package.

Photocatalytic Activity Evaluation

Photocatalytic performance was evaluated for the selective oxidation of BA into BAL in a batch reactor. The reactor setup was described in our earlier reports.^{1, 2} For each experiment, 5 or 10 mg of photocatalyst was suspended in 10 mL of BA (1 mmol L⁻¹) with acetonitrile as the solvent. The reaction system was magnetically stirred throughout the experiment and was equilibrated for 1 h before irradiation at 455 nm with a 0.3-or 0.45-watt LED lamp. The temperature inside the reaction system was maintained at 25 °C with immersion inside a water bath. After 6 or 10 h of irradiation, 0.15 mL aliquot was collected and filtered through a nylon filter to be analyzed with a gas chromatograph (GC-2010 Shimadzu) equipped with a flame ionization detector. The photocatalytic performance, i.e., BA conversion, BAL yield, and BAL selectivity, was calculated using the following equations.

$$\text{Conversion (\%)} = \left(\frac{C_0 - C_r}{C_0} \right) \times 100 \quad (1)$$

$$\text{Yield (\%)} = \left(\frac{C_p}{C_0} \right) \times 100 \quad (2)$$

$$\text{Selectivity (\%)} = \left(\frac{C_p}{C_0 - C_r} \right) \times 100 \quad (3)$$

$$\text{Aromatic balance (\%)} = \left(\frac{C_r + C_p}{C_0} \right) \times 100 \quad (4)$$

where C₀ is the initial BA concentration (mmol L⁻¹). C_r and C_p are the concentration of reactant (BA) and product (BAL) when sampling, respectively. Scavenging experiments were conducted to identify the reactive species responsible for yielding BAL. 1,4-benzoquinone (BQ), 5,5-dimethyl-1-pyrroline N-oxide (DMPO),

and *t*-Butanol (0.5 mmol L^{-1}) were added separately to the reaction system once light-exposed to scavenge superoxide radical ($\bullet\text{O}_2^-$) and hydroxyl radical ($\bullet\text{OH}$), respectively. To scavenge holes, KI and TEMPO were used. TEMP and NaN_3 were used to scavenge singlet oxygen ($^1\text{O}_2$). Meanwhile, AgNO_3 was used to scavenge electrons. To scavenge $\bullet\text{OH}$ radical, terephthalic acid (TA) assay was also performed by suspending 5 mg of photocatalyst powder in 50 mL of an aqueous solution containing 0.01 M NaOH and 5 mM TA. The mixture was stirred in the dark for 30 min before light exposure. Subsequently, 5 mL samples were taken after 1 h and centrifuged for fluorescence spectroscopy analysis. To assess the reusability of the photocatalysts, they were collected after each cycle, washed with water prior to drying and reused for three consecutive runs with a fresh BA solution.

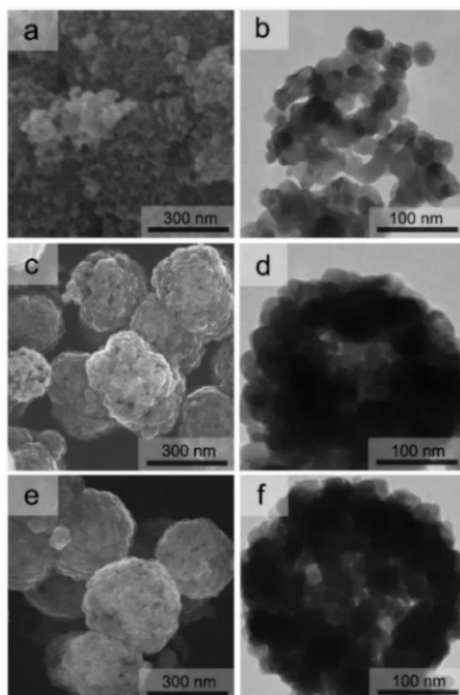


Figure S1. SEM and TEM images of (a and b) CuO-0.5AA, (c and d) Cu_2O -0.5AA, and (e and f) Cu_2O -1AA.

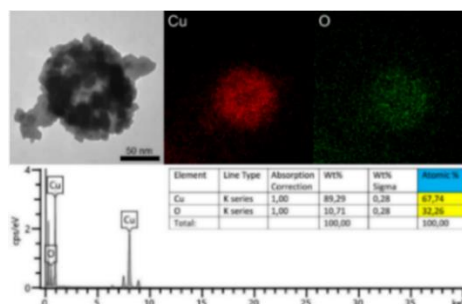


Figure S2. TEM image of Cu_2O -0.5AA with the corresponding element maps and EDX.

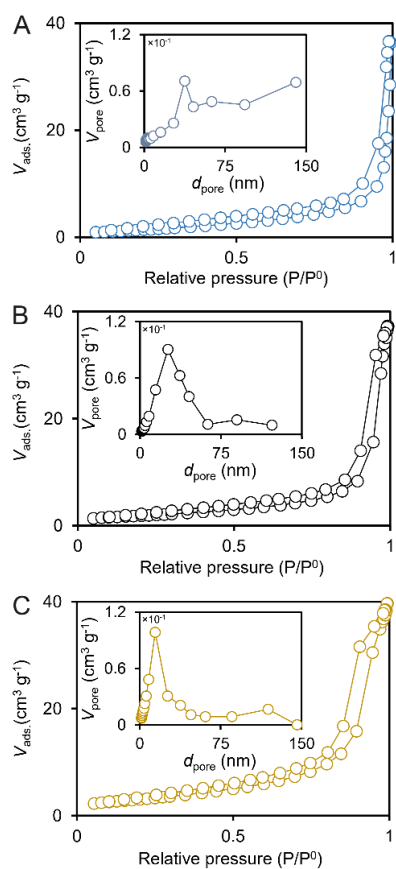


Figure S3. N_2 adsorption-desorption isotherm of (A) CuO-0AA (9 m² g⁻¹), (B) Cu₂O-0.5AA (10 m² g⁻¹), and (C) Cu₂O-1AA (14 m² g⁻¹) and their corresponding pore size distribution shown in the inset.

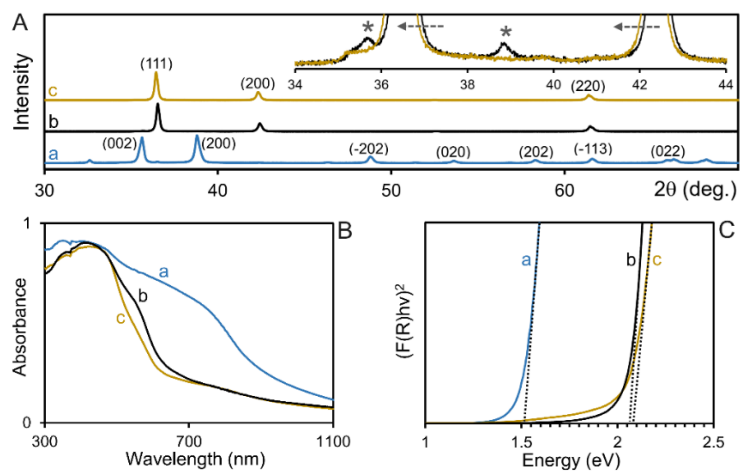


Figure S4. (A) X-ray diffraction patterns, (B) diffuse reflectance spectra, and (C) Tauc's plots of (a) CuO-0AA, (b) Cu₂O-0.5AA, and (c) Cu₂O-1AA.

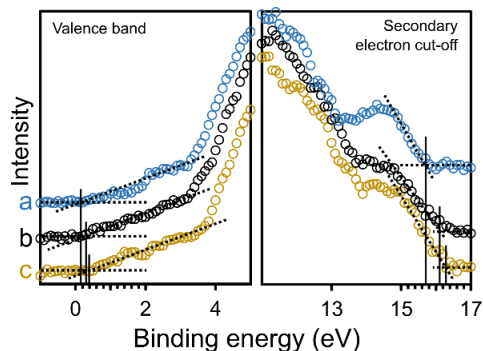


Figure S5. UV photoelectron spectra of (a) CuO-0AA, (b) Cu₂O-0.5AA, and (c) Cu₂O-1AA.

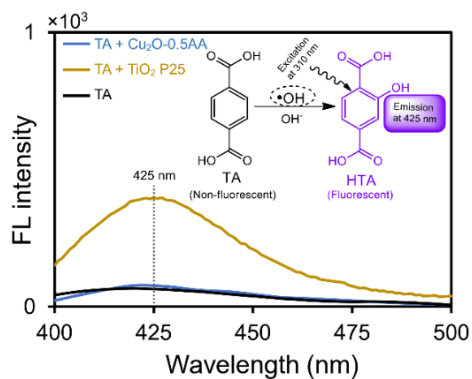


Figure S6. Fluorescence emission of the HTA solution produced from the reaction of TA with photogenerated •OH radicals. Cu₂O-0.5AA does not produce •OH radicals, as indicated by its spectrum, which is almost identical to that of the TA solution.

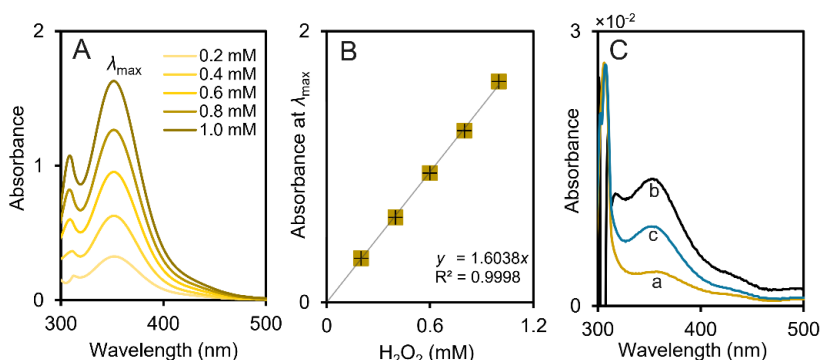


Figure S7. UV-Vis absorption intensity of different standard concentrations of H₂O₂ determined using the iodometric method. (B) Linear fitting for standard H₂O₂ concentrations. (C) UV-Vis absorption spectra for (a) CuO-0AA, (b) Cu₂O-0.5AA, and (c) Cu₂O-1AA.

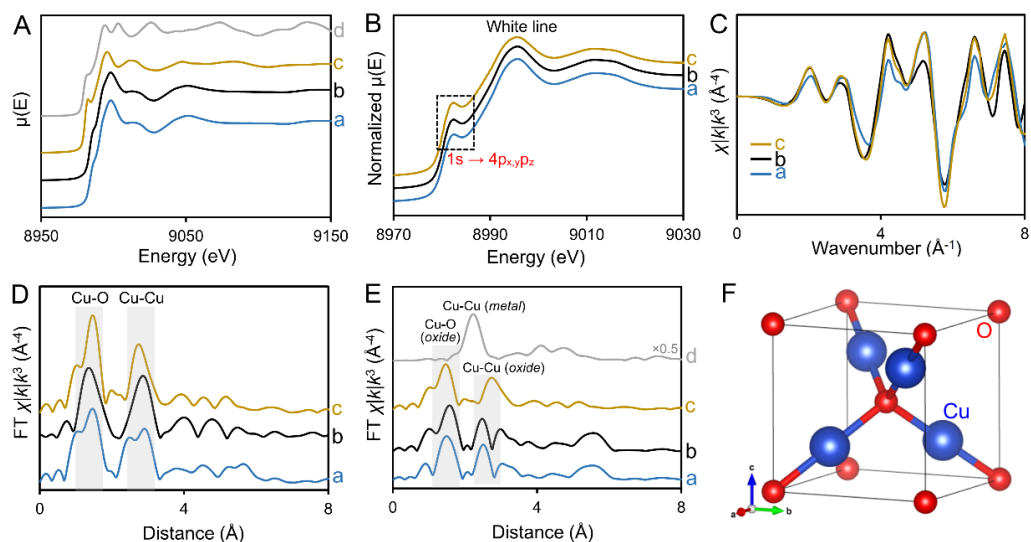


Figure S8. (A) XANES spectra of reference compounds: (a) Cu(OH)₂, (b) CuO, (c) Cu₂O, and (d) Cu foil. (B) XANES spectra of (a) Cu₂O-0.5AA, (b) Cu₂O-1AA, and (c) Cu₂O. (C) XAFS and (D) FT-XAFS spectra of (a) Cu₂O-0.5AA, (b) Cu₂O-1AA, and (c) Cu₂O. (E) FT-XAFS of reference compounds: (a) Cu(OH)₂, (b) CuO, (c) Cu₂O, and (d) Cu foil. (F) The unit cell of cubic Cu₂O.

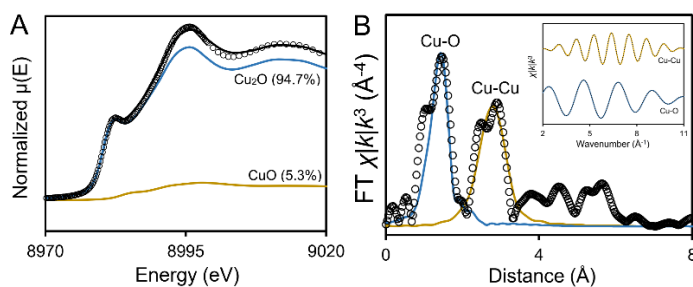


Figure S9. (A) Comparison of near-edge spectrum (circles) and fitted spectrum (black line) of Cu₂O-0.5AA with colored lines showing the portions of components making up the spectrum. (B) Comparison of XAFS spectrum (circles) and fitted spectra (colored lines) of Cu cations in Cu₂O-0.5AA coordinated with neighboring atoms.

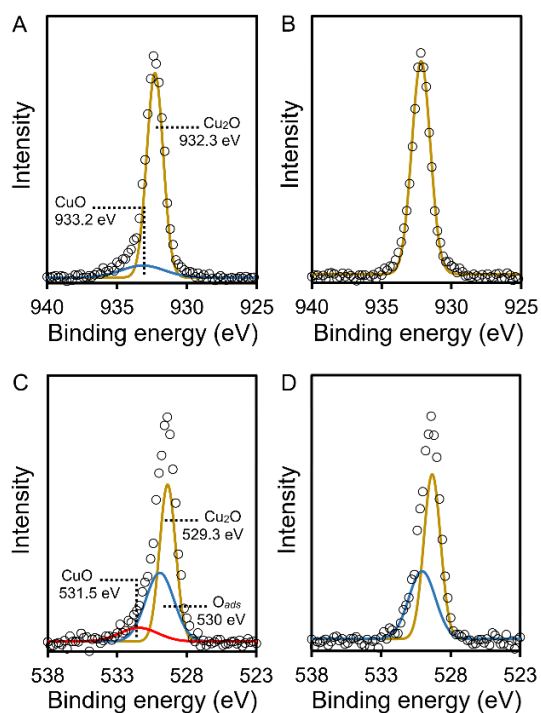


Figure S10. High-resolution XPS spectra at the Cu $2p_{3/2}$ region of (A) Cu_2O -0.5AA and (B) Cu_2O -1AA and O 1s region of (C) Cu_2O -0.5AA and (D) Cu_2O -1AA.

Table S1. Reusability tests for the BA oxidation with Cu_2O -0.5AA.

	Run	BA conv. (%)	BAL yield (%)	BAL sel. (%)
Stored for 2 months	1	21	10	48
	2	23	10	43
	3	16	8	50
	4	18	8	44
Stored for 17 months		19	10	52

Conditions: BA (1 mmol L^{-1} , 0.01 mmol), photocatalyst (0.5 g L^{-1} , 5 mg), and reaction time (6 h).

Table S2. Partial oxidation of BA over Cu_2O -0.5AA in the presence of scavengers.

Scavenger	BA conv. (%)	BAL yield (%)	BAL sel. (%)
none	18	9	50
none (O_2 flow 25 mL min^{-1} , 1 h)	25	12	48
none (degassing, 30 min; Ar flow 25 mL min^{-1} , 1 h)	0	0	0
Ag^+	7	4	57
I^-	15	8	53
BQ	10	5	50
DMPO	7	4	57
<i>t</i> -butanol	17	9	53
TEMPO	4	0	0
TEMP	16	9	56
NaN_3	19	9	47

Conditions: BA (1 mmol L^{-1} , 0.01 mmol), scavenger (5 mmol L^{-1} , 0.05 mmol), photocatalyst (0.5 g L^{-1} , 5 mg), and reaction time (6 h).

Table S3. Partial oxidation of BA over Cu₂O-1AA in the presence of scavengers.

Scavenger	BA conv. (%)	BAL yield (%)	BAL sel. (%)
none	12	4	33
none (O ₂ flow 25 mL min ⁻¹ , 1 h)	16	7	43
none (degassing, 30 min; Ar flow 25 mL min ⁻¹ , 1 h)	0	0	0
Ag ⁺	8	4	50
I ⁻	10	5	50
BQ	6	3	50
DMPO	5	2	40
<i>t</i> -butanol	13	5	38
TEMPO	2	0	0
TEMP	11	4	36
NaN ₃	12	4	33

Conditions: BA (1 mmol L⁻¹, 0.01 mmol), scavenger (5 mmol L⁻¹, 0.05 mmol), photocatalyst (0.5 g L⁻¹, 5 mg), and reaction time (6 h).

References

(1) Giannakoudakis, D. A.; Qayyum, A.; Barczak, M.; Colmenares-Quintero, R. F.; Borowski, P.; Triantafyllidis, K.; Colmenares, J. C. Mechanistic and kinetic studies of benzyl alcohol photocatalytic oxidation by nanostructured titanium(hydro)oxides: Do we know the entire story? *Applied Catalysis B: Environmental* **2023**, *320*, 121939.

(2) Qayyum, A.; Giannakoudakis, D. A.; Łomot, D.; Colmenares-Quintero, R. F.; LaGrow, A. P.; Nikiforow, K.; Lisovytskiy, D.; Colmenares, J. C. Tuning the physicochemical features of titanium oxide nanomaterials by ultrasound: Elevating photocatalytic selective partial oxidation of lignin-inspired aromatic alcohols. *Ultrasonics Sonochemistry* **2023**, *94*, 106306.