Supporting Information

Facet-Specific Photocatalytic Activity Enhancement of Cu$_2$O Polyhedra Functionalized with 4-Ethynylanaline Resulting from Band Structure Tuning

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Chemicals. Anhydrous copper (II) chloride (CuCl$_2$, 97%, Sigma–Aldrich), hydroxylamine hydrochloride (NH$_2$OH·HCl, 99%, Sigma–Aldrich), sodium hydroxide (NaOH, 98.2%, Mallinckrodt), sodium dodecyl sulfate (NaC$_{12}$H$_{25}$SO$_4$, 100%, Mallinckrodt), sodium oxalate (Na$_2$C$_2$O$_4$, 99.5%, Sigma–Aldrich), chromic (VI) acid (CrO$_3$, 99.5%, Acros Organics), methyl orange (C$_{14}$H$_{14}$N$_3$NaO$_3$S, Hayashi Pure Chemical), and 4-ethynylaniline (HC≡CC$_6$H$_4$NH$_2$, 97%, Acros Organics) were used as received without further purification. Ultrapure distilled and deionized water (18.3 MΩ) was used for all solution preparations. Sodium sulfate (Na$_2$SO$_4$, 99%, Sigma–Aldrich) was used as an electrolyte solution for electrochemical measurements. A spin-trapping reagent DMPO (5,5-dimethyl-1-pyrroline-N-oxide, 97%, Matrix) needs to be treated with activated carbon for purification.

Synthesis of Cu$_2$O Crystals. For the synthesis of cubes and rhombic dodecahedra, after adding 0.087 g of SDS powder to sample vial, 8.92 and 6.92 mL of deionized water were respectively added to each sample vial to dissolve the SDS powder, and 0.5 mL of 0.1 M CuCl$_2$ solution was injected. The sample vials were placed in a water bath set at 30–32 ºC. Next, 0.18 mL of 1.0 M NaOH solution was added under vigorous stirring. The solution became light blue immediately due to the formation of Cu(OH)$_2$ precipitate. Finally, 0.4 and 2.4 mL of 0.1 M NH$_2$OH·HCl solution was quickly injected in 5 s respectively to make cubes and rhombic dodecahedra. After stirring for 20 s, the vials were kept in the water bath for 50 min for crystal growth. The total solution volume in each vial is 10 mL. The concentrations of Cu$^{2+}$ ions and SDS surfactant in the final solution are $1.0 \times 10^{-3}$ M and $3.0 \times 10^{-2}$ M.

For the synthesis of octahedra, after adding 0.087 g of SDS powder to a sample vial, 9.05 mL of deionized water was added to dissolve the SDS powder, and 0.1 mL of 0.1 M CuCl$_2$ solution was injected. Next, 0.2 mL of 1.0 M NaOH solution was added under vigorous stirring. The solution became light blue immediately. Finally, 0.65 mL of 0.2 M NH$_2$OH·HCl solution was quickly injected in 3 s. After stirring for 10 s, the vial was kept at room temperature for 30 min for the growth of nanocrystals.
The total solution volume in the vial is 10 mL. The concentrations of Cu\(^{2+}\) ions and SDS surfactant in the final solution are \(2.0 \times 10^{-4}\) M and \(3.0 \times 10^{-2}\) M.

After the reaction, the products were centrifuged at 6000 rpm for 5 min and washed with water and ethanol in 1:1 volume ratio several times. After purification, particles were dried by purging nitrogen for storage.

**Electron Paramagnetic Resonance Analysis.** DMPO (5,5-dimethyl-1-pyrroline N-oxide) is a common spin-trapping reagent used to detect the formation of radicals. 0.1 M DMPO was prepared by adding 67.9 mg of DMPO to 6 mL of deionized water. The DMPO solution was injected through 2 mL of activated carbon over a 0.45 \(\mu\)m syringe filter for three times to purify DMPO. After purifying DMPO, the synthesized Cu\(_2\)O crystals were dispersed in 1 mL of deionized water, then 1 mL of 0.1 M DMPO was added into the solution. The solution was irradiated by a 500 W Xenon lamp with stirring for 3 min and sent for EPR analysis immediately. The settings of EPR instrument were: center field 3500 G, sweep width 100 G, sampling time 20.3 ms, field modulation amplitude 0.16 G, field modulation frequency 100 kHz, microwave frequency 9.8 GHZ, microwave power 15 mW, receiver gain 30, and receiver time constant 327.7 ms.

**Figure S1.** SEM images of the synthesized Cu\(_2\)O (a) rhombic dodecahedra, (b) octahedra, and (c) cubes.

**Figure S2.** Size distribution histograms of the synthesized Cu\(_2\)O (a) rhombic dodecahedra, (b) octahedra, and (c) cubes.
Table S1. Calculated numbers of surface copper atoms of each Cu₂O shape weighing 10 mg and concentrations and weights of 4-EA molecules having different surface copper atom to 4-EA ratios.

|                  | RD  | Octahedra | Cubes |
|------------------|-----|-----------|-------|
| Size (nm)        | 230 | 330       | 233   |
| Weight (mg)      | 10  | 10        | 10    |
| Surface area (nm²) | 4.35 x 10¹⁶ | 5.25 x 10¹⁶ | 4.29 x 10¹⁶ |
| Surface Cu atoms | 3.37 x 10¹⁷ | 7.49 x 10¹⁷ | 4.71 x 10¹⁷ |
| Surface Cu atoms : 4-EA | 1:1000 | 1:500 | 1:100 | 1:1000 | 1:500 | 1:100 |
| C₄ of 4-EA       | 0.0560 | 0.0280 | 0.0056 | 0.1244 | 0.0622 | 0.0012 |
| amount of 4-EA (mg) | 66 | 32.8 | 6.6 | 145.8 | 7.29 | 14.6 | 91.7 | 45.9 | 9.2 |

Table S2. Weights of different Cu₂O particles having a fixed surface area of 0.03 m².

|                  | RD  | Octahedra | Cubes |
|------------------|-----|-----------|-------|
| Size (nm)        | 230 | 330       | 233   |
| Surface area (nm²) | 224435.7 | 188620.3 | 325734 |
| Volume (nm³)     | 8603368 | 5989500 | 12649337 |
| Fixed area (m²)  | 0.03 | 0.03 | 0.03 |
| Number of nanoparticles | 1.34 x 10¹¹ | 1.59 x 10¹¹ | 9.21 x 10¹⁰ |
| Total volume (nm³) | 1.15 x 10¹⁸ | 9.53 x 10¹⁷ | 1.17 x 10¹⁸ |
| Weight (mg)      | 6.90 | 5.72 | 6.99 |
Figure S3. (a) TGA plots of Cu₂O cubes and 4-EA-modified Cu₂O cubes (1:100 sample) performed under air. (b) The corresponding DSC plots.

Figure S4. (a–d) UV–vis absorption spectra of methyl orange vs. irradiation time using (a) pristine and (b–d) 4-EA-modified Cu₂O rhombic dodecahedra as the photocatalysts with surface Cu atoms to 4-EA molar ratios of 1:1000 to 1:100.
Figure S5. (a–d) UV–vis absorption spectra of methyl orange as a function of irradiation time using (a) pristine and (b–d) 4-EA-modified Cu$_2$O octahedra as the photocatalysts with surface copper atoms to 4-EA molar ratios from 1:1000 to 1:100.

Figure S6. (a–d) UV–vis absorption spectra of methyl orange as a function of irradiation time using (a) pristine and (b–d) 4-EA-modified Cu$_2$O cubes as the photocatalysts with surface copper atoms to 4-EA molar ratios from 1:1000 to 1:100.
**Figure S7.** SEM images of Cu$_2$O cubes (a–d) before and (e–h) after the photocatalysis experiment. (a, e) Pristine Cu$_2$O and (b–h) 4-EA-modified Cu$_2$O with surface copper atoms to 4-EA molar ratios of (b, f) 1:1000, (c, g) 1:500, and (d, h) 1:100.

**Figure S8.** XRD patterns of pristine and 4-EA-modified Cu$_2$O (a) rhombic dodecahedra, (b) octahedra, and (c) cubes before and after the photocatalytic experiment. Cu$_2$O particles with a surface Cu atoms to 4-EA molar ratio of 1:1000 were used here.
**Figure S9.** FT-IR spectra of 4-EA-modified Cu₂O octahedra (1:100 sample) before and after the photocatalysis experiment. The peak from O–H groups is apparent possibly due to residual moisture on the samples.

**Figure S10.** EPR spectra of photoirradiated DPO and 4-EA-functionalized Cu₂O cubes. The diamonds indicate signals from hydroxyl radicals. Residual signals have been recorded for DMPO due to incomplete DMPO impurity removal.

**Table S3.** Charge transfer resistances ($R_{CT}$) of the pristine and 4-EA-modified Cu₂O crystals.
Figure S11. (a, c, e) UV–vis spectra of the pristine and 4-EA-modified Cu$_2$O crystals. (b, d, f) Tauc plots of the pristine and 4-EA-modified Cu$_2$O crystals.

Table S4. Calculated valence band and conduction band positions of various Cu$_2$O crystals in Ag/AgCl and RHE scales. The band gap values of different Cu$_2$O crystals are determined from the Tauc plots.

| Cu$_2$O | vs. Ag/AgCl | vs. RHE |
|---------|-------------|---------|
|        | $E_v$ | $E_c$ | $E_v$ | $E_c$ |
| Cubes  | $-0.18$ | $-2.07$ | $0.39$ | $-1.50$ |
| Cubes$_{4-\text{EA}}$ | $0.56$ | $-1.21$ | $1.13$ | $-0.64$ |
| Octahedra | $0.34$ | $-1.70$ | $0.91$ | $-1.13$ |
| Octahedra$_{4-\text{EA}}$ | $0.41$ | $-1.48$ | $0.98$ | $-0.91$ |
| RD     | $0.61$ | $-1.44$ | $1.18$ | $-0.87$ |
| RD$_{4-\text{EA}}$ | $1.34$ | $-0.71$ | $1.91$ | $-0.14$ |
Figure S12. Calculations for the surface area and volume of the synthesized Cu$_2$O (a) cubes, (b) octahedra, and (c) rhombic dodecahedra.