## Electronic Supplementary Information

## Facet-Dependent Photocatalytic Properties of Cu<sub>2</sub>O Crystals Probed by Electron, Hole and Radical Scavengers

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## Synthesis of Cu<sub>2</sub>O Crystals

Cu<sub>2</sub>O crystals were prepared in aqueous solution according to our previous procedures.<sup>6,7</sup> For the synthesis of nanocubes and octahedra, 9.55 and 9.05 mL of deionized water were respectively added to sample vials. After adding 0.087 g of sodium dodecyl sulfate (SDS) powder, 0.1 mL of 0.1 M CuCl<sub>2</sub> solution was injected under vigorous stirring. Next, 0.2 mL of 1.0 M NaOH solution was introduced. Finally, 0.15 and 0.65 mL of 0.2 M NH<sub>2</sub>OH·HCl were quickly injected to vials for cubes and octahedra in 5 s. The total volume in each vial is 10 mL. The vials were left at room temperature for 2 h to obtain the particles. After the reaction, the orange precipitate was collected by centrifugation at 7500 rpm for 5 min and washed with water and ethanol in 1:1 volume ratio several times.

For the synthesis of rhombic dodecahedra, 6.92 mL of deionized water was added to a vial. The vial was placed in a water bath set at 32–34 °C. Then 0.5 mL of 0.1 M CuCl<sub>2</sub> solution and 0.087g of SDS powder were added to the vial with vigorous stirring. After complete dissolution of SDS powder, 0.18 mL of 1.0 M NaOH solution was introduced. Finally, 2.4 mL of 0.1 M NH<sub>2</sub>OH·HCl solution was quickly injected to the vial in 3 s, and the vial was kept in the water bath for 1 h for nanocrystal growth. After the reaction, the sample was washed as described above.



**Fig. S1** Size distribution histograms of the synthesized  $Cu_2O(a)$  cubes, (b) octahedra, and (c) rhombic dodecahedra.



**Fig. S2.** XRD patterns of (a–c) Cu<sub>2</sub>O rhombic dodecahedra, (d, e) octahedra, and (f, g) cubes (a, d, f) before and after (b) 30 min and (c, e, g) 90 min of the isopropanol photocatalysis experiment. (i) Standard XRD pattern of Cu<sub>2</sub>O. All XRD patterns look the same because a dense amount of particles was used in these measurements.



**Fig. S3** (a-f) UV-vis absorption spectra of MO as a function of irradiation time using Cu<sub>2</sub>O (a, b) cubes, (c, d) octahedra, and (e, f) rhombic dodecahedra as photocatalysts in the presence of (a, c, e) electron and (b, d, e) hole scavengers.



**Fig. S4** UV–vis absorption spectra of methyl orange as a function of irradiation time using rhombic dodecahedra as the photocatalyst in the presence of 10  $\mu$ mole of (a) electron and (b) hole scavengers.



**Fig. S5** (a–e) UV–vis absorption spectra of MO as a function of irradiation time using  $Cu_2O$  cubes, octahedra, and rhombic dodecahedra as photocatalysts in the presence of different volumes of isopropanol acting as 'OH scavenger. (f–h) Extent of photodegradation of MO by  $Cu_2O$  cubes, octahedra, and rhombic dodecahedra with the addition of isopropanol as 'OH radical scavenger.



Fig. S6. (a-c) SEM images of Cu<sub>2</sub>O (a) cubes, (b) octahedra, and (c) rhombic dodecahedra after the photocatalysis experiment. (d-g) TEM images of single Cu<sub>2</sub>O rhombic dodecahedron after the photocatalysis experiment and the corresponding SAED patterns. Viewing zone axes are indicated and marked in the schematic drawings showing the orientations of the rhombic dodecahedra.



**Fig. S7** (a, b, c) UV–vis absorption spectra of MO as a function of irradiation time using Cu<sub>2</sub>O (a) cubes, (b) octahedra, and (c) rhombic dodecahedra as the photocatalysts in the presence of benzoquinone as  $O_2^-$  scavenger. (d) Summary of photodegradation of MO on Cu<sub>2</sub>O crystals using benzoquinone as  $O_2^-$  scavenger with absorbance measured at 464 nm.



**Fig. S8** (a) Full XPS spectra of Cu<sub>2</sub>O cubes, octahedra, and rhombic dodecahedra. (b) Expanded XPS spectra showing the Cu 2p peaks. (c) Expanded XPS spectrum showing the Cu 3p and Cu 3s peaks.