

## Electronic Supplementary Information

# Crystal-facet-dependent effect of polyhedral Cu<sub>2</sub>O microcrystals on photocatalytic activity

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## 1. Experimental Section

**1.1 Synthesis of octahedral Cu<sub>2</sub>O microcrystals.** All chemicals used in our experiment were of analytical grade and used without further purification. Aqueous solutions were prepared using ultrapure water. In a typical experiment, Cu(CH<sub>3</sub>COO)<sub>2</sub> (2.9946 g) was dissolved in deionized water (20 mL) under a constant stirring at 70 °C for 2 min. A dark precipitate was produced when a sodium hydroxide solution (10 mL, 9 M) was added dropwise to the above solution. After being stirred for 5 min, D-glucose powder (0.3 g) was added into the dark precursor with a constant stirring for another 5 min at 70 °C. When the reaction temperature enhanced up to 70 °C again, we collected the products at 60 min. Afterward, the obtained particles were centrifuged at 5000 rpm for 1 min (XIANYI TG16-WS centrifuge). The precipitates were centrifuged twice more in deionized water and anhydrous ethanol, and finally were dried at 70 °C for 12 hours in a vacuum oven.

**1.2 Synthesis of 14-facet polyhedral Cu<sub>2</sub>O microcrystals.** All chemicals used in our experiment were of analytical grade and used without further purification. Aqueous solutions were prepared using ultrapure water. In a typical procedure, CuSO<sub>4</sub> (1.25 g) was dissolved in deionized water (50 mL) using a beaker under a constant stirring at 55 °C for 2 min. A dark precipitate was produced when a sodium hydroxide solution (1.2 g, 5 mL H<sub>2</sub>O)

was added dropwise to the above solution. After being stirred for 5 min, D-(+)-glucose powder (0.2 g) was added into the dark precursor with a constant stirring for another 20 min at 55 °C. The dark precipitate immediately turned brown red, and gradually turned dark red at 70 °C, and then was allowed to cool to room temperature naturally. Afterward, the obtained particles were centrifuged at 5000 rpm for 1min (XIANYI TG16-WS centrifuge). The precipitates were centrifuged twice more in deionized water and anhydrous ethanol, respectively. And finally were dried at 70 °C for 12 hours in a vacuum oven.

**1.3 Synthesis of 26-facet truncated edge cubic Cu<sub>2</sub>O microcrystals.** All chemicals used in our experiment were of analytical grade and used without further purification. Aqueous solutions were prepared using ultrapure water. In a typical procedure,<sup>24</sup> Cu(CH<sub>3</sub>COO)<sub>2</sub> (2.9946 g) was dissolved in deionized water (50 mL) using a beaker under a constant stirring at 70 °C for 2 min. A dark precipitate was produced when a sodium hydroxide solution (3.6 g, 30 mL H<sub>2</sub>O) was added dropwise to the above solution. After being stirred for 5 min, D-(+)-glucose powder (0.6 g) was added into the dark precursor with a constant stirring for another 20 min at 70 °C. The dark precipitate immediately turned brown red, and gradually turned dark red at 70 °C, and then was allowed to cool to room temperature naturally. Afterward, the obtained particles were centrifuged at 5000 rpm for 1min (XIANYI TG16-WS centrifuge). The precipitates were centrifuged twice more in deionized water and anhydrous ethanol, respectively. And finally were dried at 70 °C for 12 hours in a vacuum oven.

**1.4 Synthesis of 26-facet truncated edge octahedral Cu<sub>2</sub>O microcrystals.** All chemicals used in our experiment were of analytical grade and used without further purification. Aqueous solutions were prepared using ultrapure water. In a typical procedure,<sup>23</sup> Cu(CH<sub>3</sub>COO)<sub>2</sub> (2.9946 g) was dissolved in deionized water (40 mL) using a beaker under a constant stirring at 70 °C for 2 min. A dark precipitate was produced when a sodium hydroxide solution (3.6 g, 10 mL H<sub>2</sub>O) was added dropwise to the above solution. After being stirred for 5 min, D-(+)-glucose powder (0.6 g) was added into the dark precursor with a constant stirring for another 60 min at 70 °C. The dark precipitate

immediately turned brown red, and gradually turned dark red at 70 °C, and then was allowed to cool to room temperature naturally. Afterward, the obtained particles were centrifuged at 5000 rpm for 1min (XIANYI TG16-WS centrifuge). The precipitates were centrifuged twice more in deionized water and anhydrous ethanol, respectively. And finally were dried at 70 °C for 12 hours in a vacuum oven.

**1.5 Synthesis of 50-facet Cu<sub>2</sub>O microcrystals partially exposed with {522} facets.** All chemicals used in our experiment were of analytical grade and used without further purification. Aqueous solutions were prepared using ultrapure water. In a typical procedure,<sup>24</sup> Cu(CH<sub>3</sub>COO)<sub>2</sub> (2.9946 g) was dissolved in deionized water (50 mL) using a beaker under a constant stirring at 70 °C for 2 min. A dark precipitate was produced when a sodium hydroxide solution (3.6 g, 30 mL H<sub>2</sub>O) was added dropwise to the above solution. After being stirred for 5 min, D-(+)-glucose powder (0.6 g) was added into the dark precursor with a constant stirring for another 5 min at 70 °C. The dark precipitate immediately turned brown red, and gradually turned dark red at 70 °C, and then was allowed to cool to room temperature naturally. Afterward, the obtained particles were centrifuged at 5000 rpm for 1min (XIANYI TG16-WS centrifuge). The precipitates were centrifuged twice more in deionized water and anhydrous ethanol, respectively. And finally were dried at 70 °C for 12 hours in a vacuum oven.

**1.6 Synthesis of 50-facet Cu<sub>2</sub>O microcrystals partially exposed with {211} facets.** All chemicals used in our experiment were of analytical grade and used without further purification. Aqueous solutions were prepared using ultrapure water. In a typical procedure,<sup>24</sup> Cu(CH<sub>3</sub>COO)<sub>2</sub> (2.9946 g) was dissolved in deionized water (50 mL) using a beaker under a constant stirring at 70 °C for 2 min. A dark precipitate was produced when a sodium hydroxide solution (3.6 g, 15 mL H<sub>2</sub>O) was added dropwise to the above solution. After being stirred for 5 min, D-(+)-glucose powder (0.6 g) was added into the dark precursor with a constant stirring for another 20 min at 70 °C. The dark precipitate immediately turned brown red, and gradually turned dark red at 70 °C, and then was allowed to cool to room temperature naturally. Afterward, the obtained particles were centrifuged at 5000 rpm for 1min (XIANYI

TG16-WS centrifuge). The precipitates were centrifuged twice more in deionized water and anhydrous ethanol, respectively. And finally were dried at 70 °C for 12 hours in a vacuum oven.

**1.7 Characterization.** The morphology of the powders was investigated by field-emission scanning electron microscopy (FE-SEM) using JEOL (JSM-7000F) at an accelerating voltage of 20 KV. The UV-vis spectra were measured by a UV/vis/NIR spectrophotometer (Hitachi U-4100).

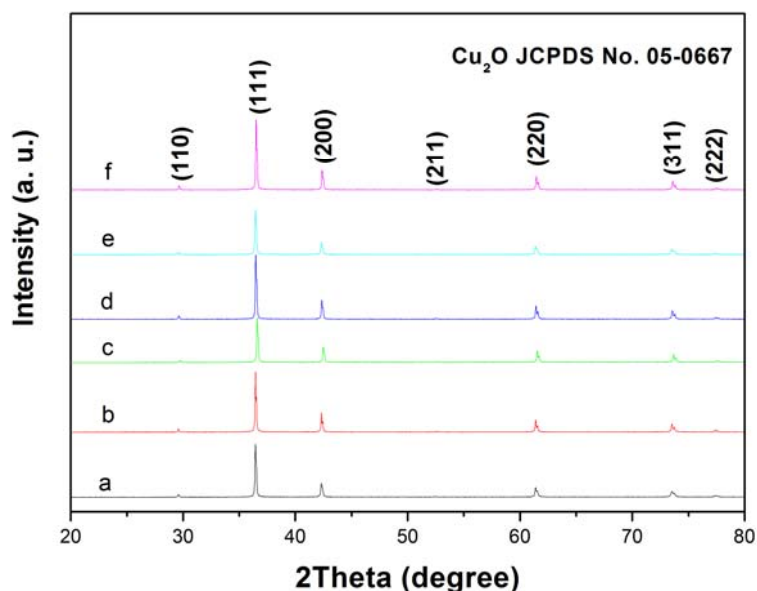
**1.8 Photocatalytic property.** The catalytic activity experiment of the different Cu<sub>2</sub>O microcrystals for the oxidation and decoloration of the methyl orange (MO) dye was carried out at room temperature. The original solution was prepared by adding 50 mL MO solution (5mg/L), and then 100 mg Cu<sub>2</sub>O powder was added into the solution to form the aqueous dispersion. Before illumination, the solution was stirred in the dark for 1 hour to evaluate the adsorption property. Afterwards, the dispersion was irradiated by a 500 W xenon lamp under magnetic stirring. At given time intervals, the dispersion was sampled and centrifuged to separate the catalyst. UV-vis absorption spectra were recorded at different intervals to monitor the reaction using a UV/vis/NIR spectrophotometer (Hitachi U-4100).

## 2. Theoretical Calculation

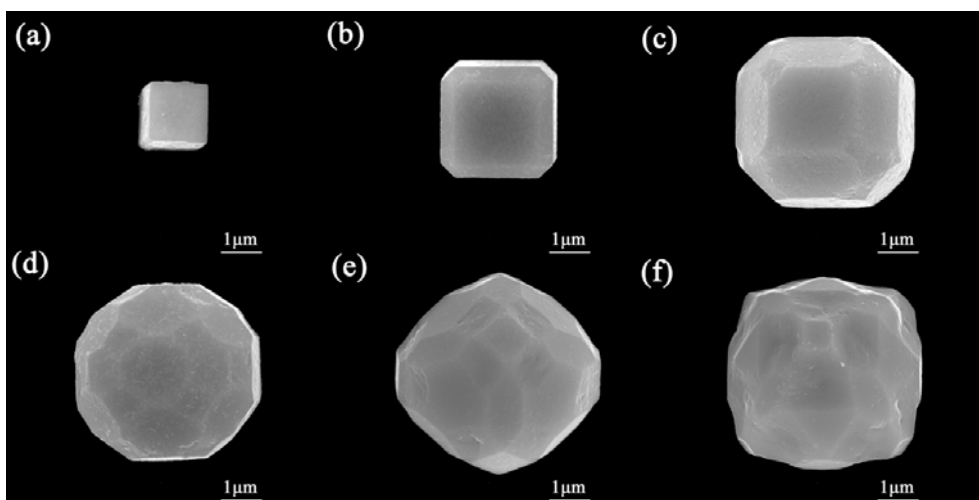
A density functional theory (DFT) calculation was performed using Dmol3 code which developed by Delley<sup>1-3</sup>. Firstly, a Cu<sub>2</sub>O crystal cell was optimized and then based on this cell, different Cu<sub>2</sub>O crystal surfaces ((522) and (211)) were cleaved out with the size of 2×2×16 (W×L×H) and periodic boundary. Next, the different crystal surfaces were optimized with no symmetry and spin polarization limitation. After optimization, the bond length and bond energy of 2 layers atoms below surface were statistic. The structure optimization and energy calculation both were performed using Perdew-Wang exchange-correlation function (PW91) based on the generalized gradient approximation (GGA). In the DFT calculation, no symmetry and spin restrictions were applied. The method of a double numerical basis set plus a polarization p-function (DNP), DFT semicore pseudopotentials (DSPP), and an

octupole scheme were used to describe the multipolar expansion of the charge density and Coulomb potential. A thermal smearing of 0.005 Hartree (0.136 eV) was set for the energy level of occupied orbitals in order for them to converge. The following criteria were used to obtain the final optimized structure: the convergence tolerance of self-consistent field (SCF) energy should be less than  $10^{-6}$  Hartree ( $2.72 \times 10^{-5}$  eV) in the conjugate gradient algorithm; the maximum displacement of an atom was less than 0.005 Å, and the force due to the displacement was less than 0.002 Hartree/Å (0.054 eV/Å).

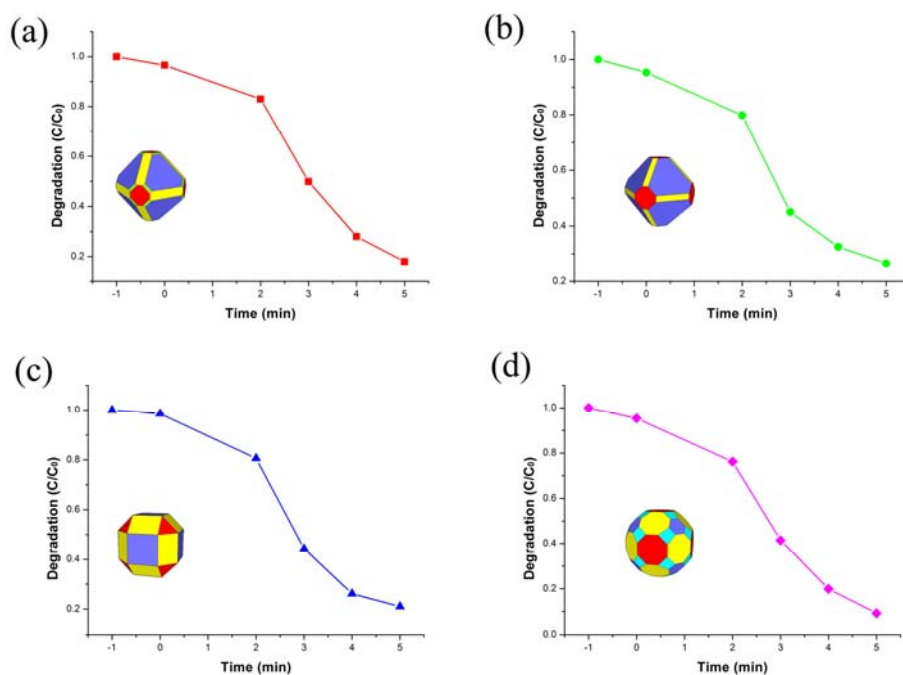
1. Delley, B., An All-Electron Numerical-Method for Solving the Local Density Functional for Polyatomic-Molecules. *J. Chem. Phys.* 1990, 92 (1), 508-517.
2. Delley, B., From molecules to solids with the DMol(3) approach. *J. Chem. Phys.* 2000, 113 (18), 7756-7764.
3. Delley, B., DMol(3) DFT studies: from molecules and molecular environments to surfaces and solids. *Comp. Mater. Sci.* 2000, 17 (2-4), 122-126.



**Fig. S1** XRD patterns of the six types of polyhedral Cu<sub>2</sub>O microcrystals as shown in Fig. 3. (a) 8-facet; (b) 14-facet; (c) 26-facet polyhedral Cu<sub>2</sub>O cubes; (d) 26-facet polyhedral Cu<sub>2</sub>O octahedra; (e) 50-facet polyhedral with high-index {522} facets; (f) 50-facet polyhedral with high-index {211} facets.



**Fig. S2** FESEM images of the products obtained by adjusting the concentration of sodium hydroxide based on synthetic process of the Synthesis of 50-facet  $\text{Cu}_2\text{O}$  microcrystals partially exposed with  $\{522\}$  facets. (a) 3.6 g (NaOH)/150 mL( $\text{H}_2\text{O}$ ) (6-facet); (b) 3.6 g/100 mL (26-facet); (c) 3.6 g/50 mL (50-facet); (d) 3.6 g/30 mL(50-facet, Fig. 3e); (e) 3.6 g/15 mL (74-facet); (f) 3.6 g/5 mL (98-facet).



**Fig. S3** A plot of the extent of photodegradation of MO by different  $\text{Cu}_2\text{O}$  catalysts at different intervals. The insets are the corresponding geometrical shapes of the  $\text{Cu}_2\text{O}$  microcrystals.