Electronic supplementary information

One-pot synthesis of etched Cu_2O cubes with exposed {110} facets with enhanced visible-light-driven photocatalytic activity

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Experimental sections

Materials

$CuCl_2{\cdot}2H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, Ethylene Diamine Tetraacetic Acid (EDTA), Ascorbic Acid (AA) and NaOH were obtained from Aladdin reagent. All chemicals used in our experiment were of analytical grade and used without further purification. Deionized water (18.25 MΩ•cm) from a MilliQ Academic water purification system (Millipore Corp.) was used in all preparations.

Preparation of the etched Cu_2O cubes

In a typical procedure, 0.5 mL of 0.1 M $CuCl_2{\cdot}2H_2O$ solution, a molar ratio of 6% $Fe(NO_3)_3{\cdot}9H_2O$ solution, and 0.025 mmol EDTA were added to 25 mL deionized water using a breaker. After 30 min, 0.5 mL of 0.4 M NaOH solution was added. Stirring for about 5 min, 0.5 mL of 0.1 M AA solution was added into the above blue solution for 1.0 h to obtain the desired products at the room temperature, and then the samples were centrifuged at 12000 rpm for 1 min (XIANYI TG16-WS centrifuged). The precipitates were collected and washed with deionized water and anhydrous ethanol many times, respectively. Finally they were dried at 60°C for 6 h in a vacuum oven.

Characterization

The crystalline phase of the samples was characterized by an X-ray diffractometer (Bruker-AXS D8 ADVANCE) with Cu-Kα

(λ=1.54060 Å) in the range (20~80°). Surface analysis for the as-prepared products was performed by an X-ray photoelectron spectroscopy (XPS) using an Al mono Kα X-ray source operated at 90 W (England, Kratos Axis Ultra DLD). The morphology of the samples was investigated by field-emission scanning electron microscopy (FESEM) using a JEOL (JSM-7000F) at an accelerating voltage of 20 KV. The energy dispersive X-ray (EDX) analysis was obtained with an Oxford INCA EDX detector installed on the JEOL JSM-7000F. The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analyses as well as selected-area electron diffraction (SAED) pattern analysis were performed on a JEOL JEM-2100 transmission electron microscope operating at an accelerating voltage of 200 kV. Sample for the TEM analysis was prepared by ultrasonic dispersion for 30 s with ethanol (1.5 mL) in a 2 mL centrifuge tube, and then the suspension was dropped onto a carbon-coated copper grid and dried in air before TEM analysis. The Brunauer–Emmett–Teller (BET) surface area of the samples were determined by nitrogen adsorption-desorption isotherm measurements at 77 K with a Micromeritics Autosorb IQ analyzer.

Photocatalytic experiments

In a typical process, the photocatalytic activities for the etched and normal Cu_2O cubes were investigated with the use of methyl orange (MO) as a pollutant. Briefly, 50 mg of the as-synthesized samples were dispersed in 50 mL MO solution (10 mg/L), respectively. At first, the mixture was irradiated with the light from a 500 W Xe lamp under constantly stirring, and then about 3 mL of the mixture solution was taken out at different time intervals. After centrifugation, the adsorption behavior of the supernatant was analyzed though a UV-Vis spectrophotometer (UV-Vis/NIR spectrophotometer (Hitachi U-4100)).

Figures

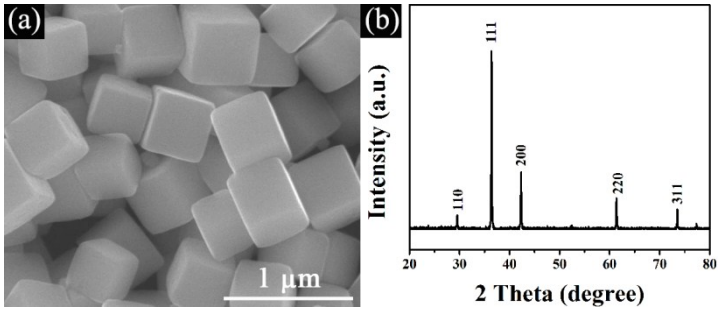


Fig. S1 FESEM image (a) and XRD pattern (b) of the normal Cu_2O cubes.

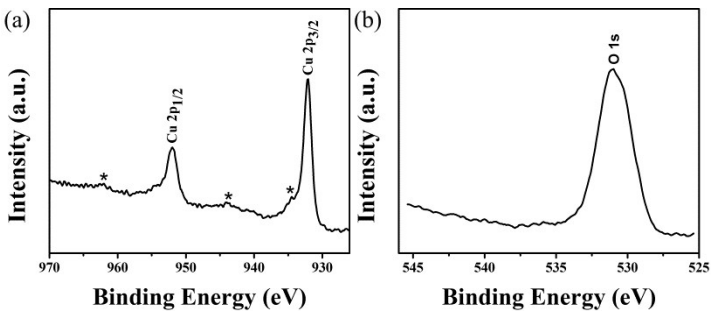


Fig. S2 XPS spectrum of the etched Cu_2O cubes: (a) Cu 2p core-level; (b) O 1s core-level.

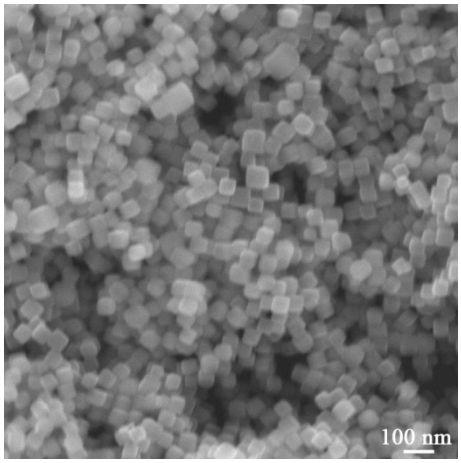


Fig. S3 FESEM image of the Cu_2O crystals without EDTA and $Fe(NO_3)_3$ added.

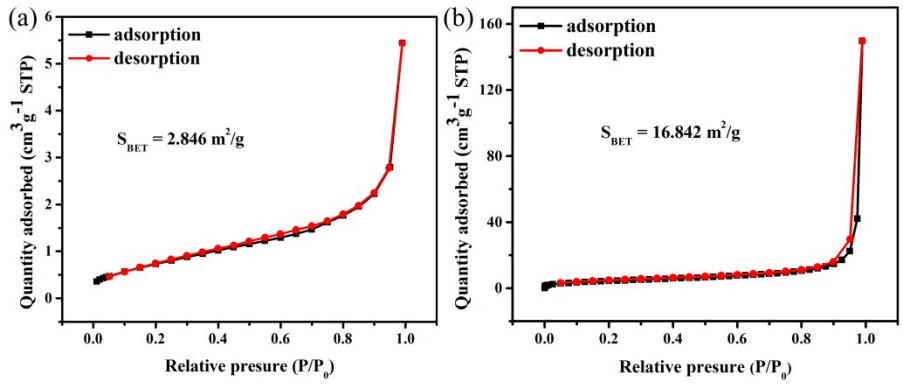


Fig. S4 Nitrogen adsorption-desorption isotherm of the normal Cu_2O cubes (a) and the etched Cu_2O cubes (b).

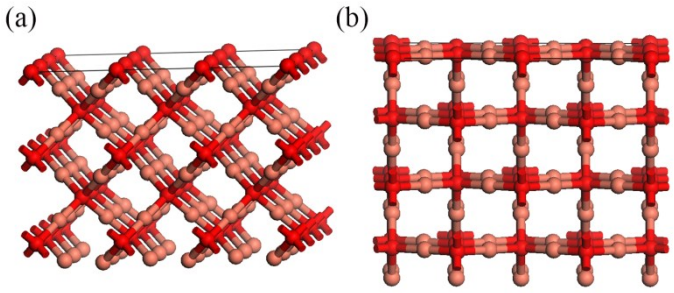
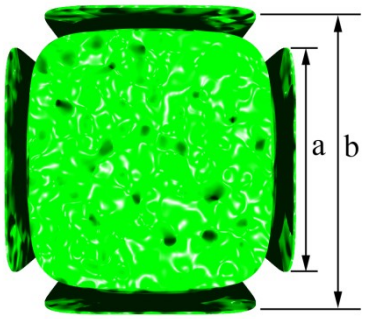


Fig. S5 Crystallographic structures of (a) the {100}, and (b) the {110} facets of Cu_2O crystals, the pinkish red and red balls represent copper and oxygen atoms, respectively.

Turnover frequency (TOF) calculations

Surface copper atoms are considered to be the active catalytic sites. For simplicity, the etched Cu_2O cubes can be seen as smooth cubes. Based on the SEM results, we can get the geometrical parameters of the etched Cu_2O cubes through statistic according to SEM images based on about 100 particles. We can calculate turnover frequency (TOF) as follows:

Turnover frequency (TOF) = (moles dye converted) / (moles of total surface copper atoms × reaction time)



a = 359 nm; b = 432 nm

$S = 432 \times 432 = 186624\ nm^2$

$S_{100} = 359 \times 359 = 128881\ nm^2$

$P_{100} = (6 \times S_{100}) \times 100\% / (6 \times S) = 69.1\%$

$P_{110} = 1 - 69.1\% = 30.9\%$

Lattice Constance: a = 0.4267 nm

The surface copper atom density:

{100} facets: $32 / (4 \times 0.4267 \times 4 \times 0.4267) = 10.98\ nm^{-2}$

{110} facets: $32 / (4 \times 0.4267 \times 4\sqrt{2} \times 0.4267) = 7.77\ nm^{-2}$

All catalysts have approximately the same total surface area of $2.8 \times 10^{15}\ nm^2$

The surface area contains mol of Cu atoms:

Normal Cu_2O cubes: $(10.98 \times 2.8 \times 10^{15}) / (6.02 \times 10^{23}) = 5.11 \times 10^{-8}$

Etched Cu_2O cubes: $(10.98 \times 2.8 \times 10^{15} \times 69.1\%) / (6.02 \times 10^{23}) + (7.77 \times 2.8 \times 10^{15} \times 30.9\%) / (6.02 \times 10^{23}) = 4.65 \times 10^{-8}$

For photocatalytic activity, the moles dye is 1.5×10^{-6}.

TOF of normal cubes = 1.5×10^{-6} mol × 0.65 / (5.11×10^{-8} mol × 1.5 h) = 12.7 h^{-1}

TOF of the etched cubes = 1.5×10^{-6} mol × 0.93 / (4.65×10^{-8} mol × 1.5 h) = 20 h^{-1}