

## Electronic Supplementary Information

### Facet-selective growth of Cu–Cu<sub>2</sub>O heterogeneous architectures

Shaodong Sun, Chuncai Kong, Hongjun You, Xiaoping Song, Bingjun Ding and Zhimao Yang\*

*School of Science, MOE Key Laboratory for Non-Equilibrium Synthesis and Modulation of Condensed Matter,  
State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, ShaanXi,  
People's Republic of China*

\*E-mail: zmyang@mail.xjtu.edu.cn

## Experimental Section

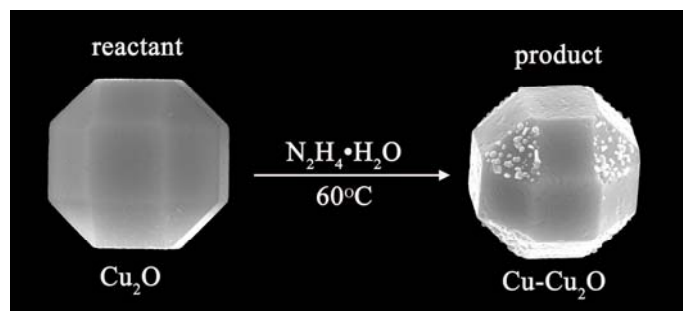
### Synthesis of polyhedral 26-facet Cu<sub>2</sub>O templates

Polyhedral 26-facet Cu<sub>2</sub>O particles were synthesized based on a template-free complex precursor solution synthesis route, which involves the reduction of Cu<sup>2+</sup>/NaOH/H<sub>2</sub>O system with D-(+)-glucose powder.<sup>16</sup> All chemicals used in our experiment were of analytical grade and used without further purification. In a typical procedure, 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. These Cu<sub>2</sub>O precipitates were separated by centrifugation, washed with deionized water and ethanol. And finally were dried at 60 °C for 12 hours in a vacuum oven.

### Synthesis of polyhedral 26-facet Cu–Cu<sub>2</sub>O heterogeneous architectures

In a typical synthesis, the as-obtained Cu<sub>2</sub>O templates (0.2 g) were added to pure water solution (60 mL) at room temperature and ambient pressure for 10 min under magnetic stirring. Then hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O) (3 mL, 50 wt%) was added into the above mixture under magnetic stirring. Subsequently, the reaction system was heated

up to 60°C for 2 min, and then allowed to cool to room temperature naturally. Afterwards, the obtained particles were separated and cleaned by repeated centrifugation with water and ethanol, and dried at 50 °C for 12 hours in a vacuum oven. Finally, the powder was taken for characterization.



**Scheme S1.** The reaction process of the formation of Cu-Cu<sub>2</sub>O heterogeneous architectures.

### Characterization

Powder X-ray diffraction (XRD) pattern was recorded on a Bruker-AXS D8 ADVANCE diffractometer operated at 40 kV voltage and 40 mA current using Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the range (20 ~ 80 °). The morphology of the products was investigated by field-emission scanning electron microscopy (FE-SEM) using JEOL (JSM-7000F) at an accelerating voltage of 20 kV. EDX analysis was obtained with an Oxford INCA Energy dispersive X-ray detector installed on the JEOL JSM-7000F. Surface analysis for the as-prepared products was performed by an X-ray photoelectron spectroscopy (England, Kratos Axis Ultra DLD) using an Al mono K $\alpha$  X-ray source operated at 90 W.

### Photocatalytic property

The catalytic activity experiments of the original 26-facet Cu<sub>2</sub>O and the as-prepared Cu-Cu<sub>2</sub>O heterodimers for the oxidation and decoloration of the methyl orange (MO) dye was carried out at room temperature. The original solution was prepared by adding 100 mL MO solution (10 mg/L), and then 0.15 g Cu<sub>2</sub>O powder was added into the solution to form the aqueous dispersion. Before illumination, the solution was vigorously stirred in the dark for 0.5 h to evaluate the adsorption property. Afterwards, the dispersion was irradiated by a 500 W xenon lamp equipped

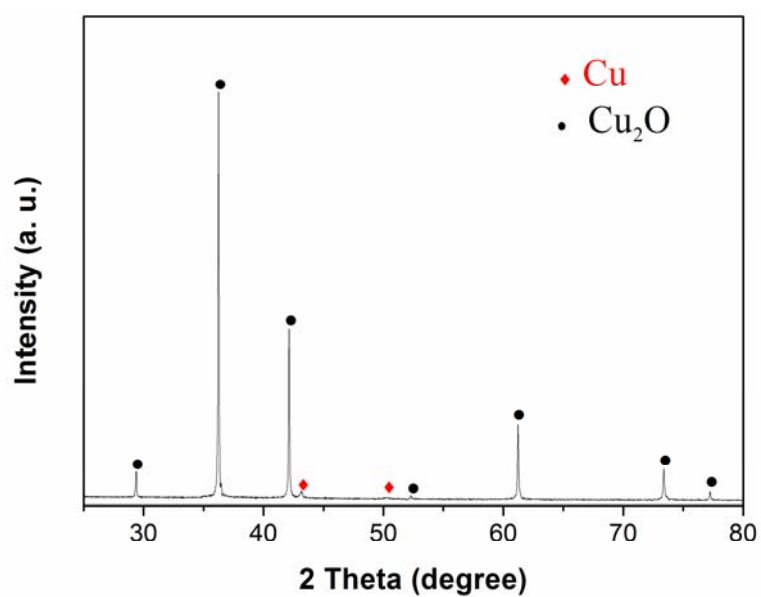
with a filter cutoff ( $\lambda \geq 420$  nm) under magnetic stirring. At given time intervals, the dispersion was sampled and centrifuged to separate the catalyst. UV-vis absorption spectra were recorded at different intervals to monitor the reaction using a UV/vis/NIR spectrophotometer (Hitachi U-4100).

### Theoretical Calculation

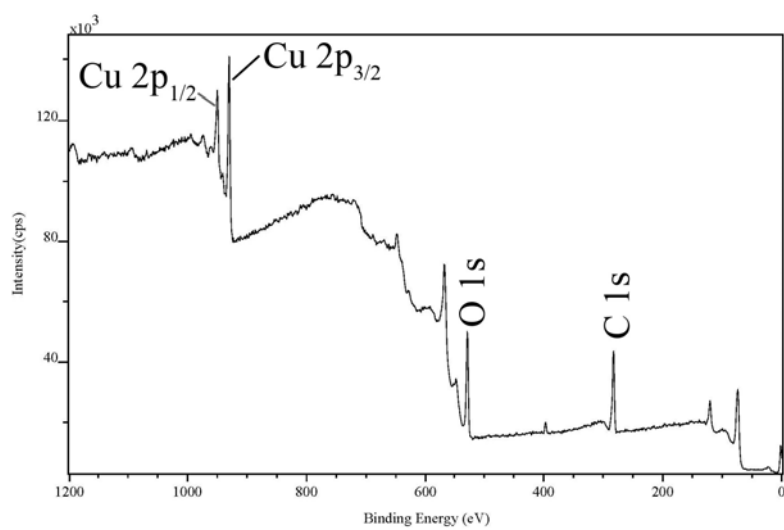
A density functional theory (DFT) calculation was performed using Dmol3 code which developed by Delley<sup>1-3</sup>. Firstly, a Cu<sub>2</sub>O crystal cell was optimized and then based on this cell, different Cu<sub>2</sub>O crystal surfaces ((100), (110) and (111)) were cleaved out with the size of 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 orbits 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<sup>-6</sup> Hartree (2.72×10<sup>-5</sup> 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*

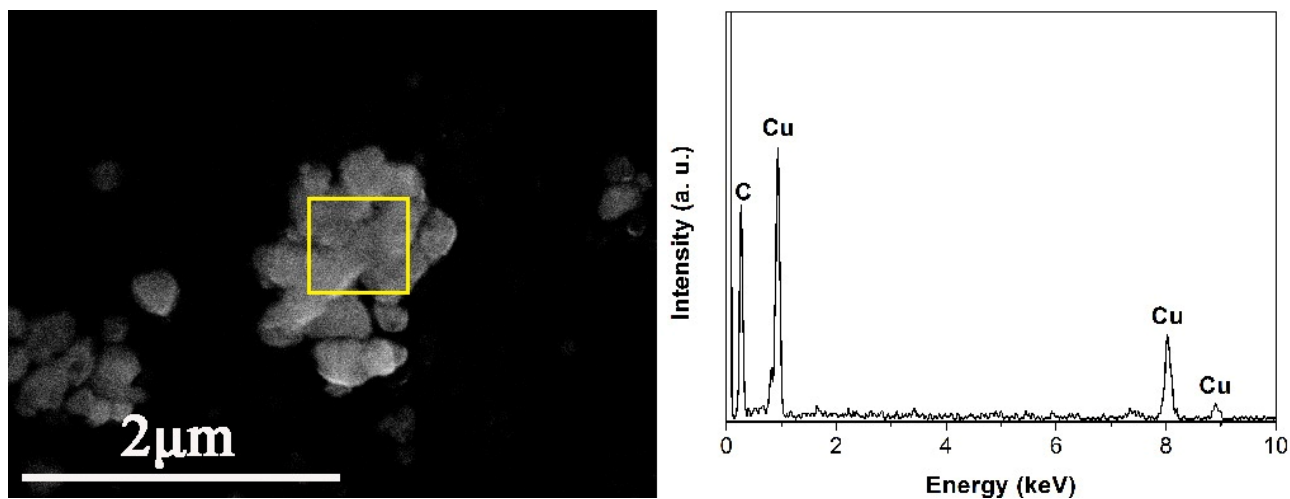
Mater Sci 2000, 17 (2-4), 122-126.



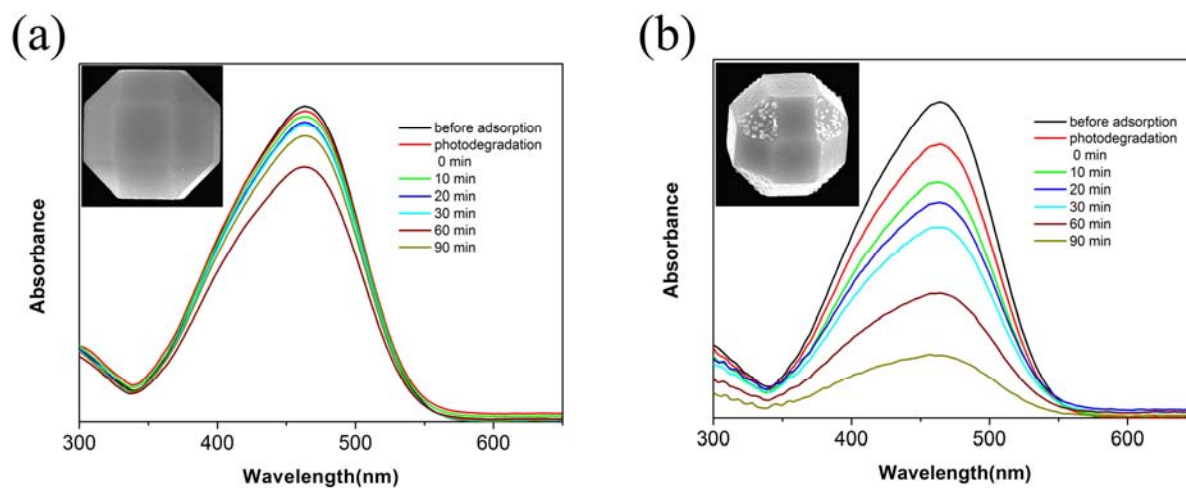
**Fig. S1** XRD pattern of the as-prepared Cu-Cu<sub>2</sub>O heterogeneous architectures.



**Fig. S2** XPS wide spectrum of the as-prepared Cu-Cu<sub>2</sub>O heterogeneous architectures.



**Fig. S3** (a) FESEM image of the separate nanoparticles; (b) The corresponding EDX spectrum of the area marked with yellow square.



**Fig. S4** (a) Absorption spectra of the solution of MO dyes in the presence of the original 26-facet Cu<sub>2</sub>O; (b) Absorption spectra of the solution of MO dyes in the presence of as-prepared Cu-Cu<sub>2</sub>O heterogeneous architectures.