Electronic Supplementary Material (ESI) for CrystEngComm

Electronic supplementary information

Etching-limited branching growth of cuprous oxide during ethanol-assisted solution synthesis

Shaodong Sun,[§] Hongjun You,[§] Chuncai Kong,[§] 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

[§] These authors contributed equally.

* Corresponding Author. E-mail: zmyang@mail.xjtu.edu.cn

Experimental Section 1

All chemicals used in our experiment were of analytical grade and used without further purification. In a typical experiment, $Cu(CH_3COO)_2$ (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. Then ethanol (30 mL) was added, when the reaction temperature enhanced up to 70 °C again, we collected the products at 1 min, 5 min, 15 min and 60 min, respectively. Afterward, the obtained particles (samples S1-S4) 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.

The crystal phase of as-prepared products was characterized by an X-ray diffractometer (SHIMADZU XRD-7000S) with Cu Kα radiation (λ = 1.54060 Å) 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.

Experimental Section 2

In a typical experiment, $Cu(CH_3COO)_2$ (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 5 min and 60 min at 70 °C. The obtained particles (samples S5, S6) 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.

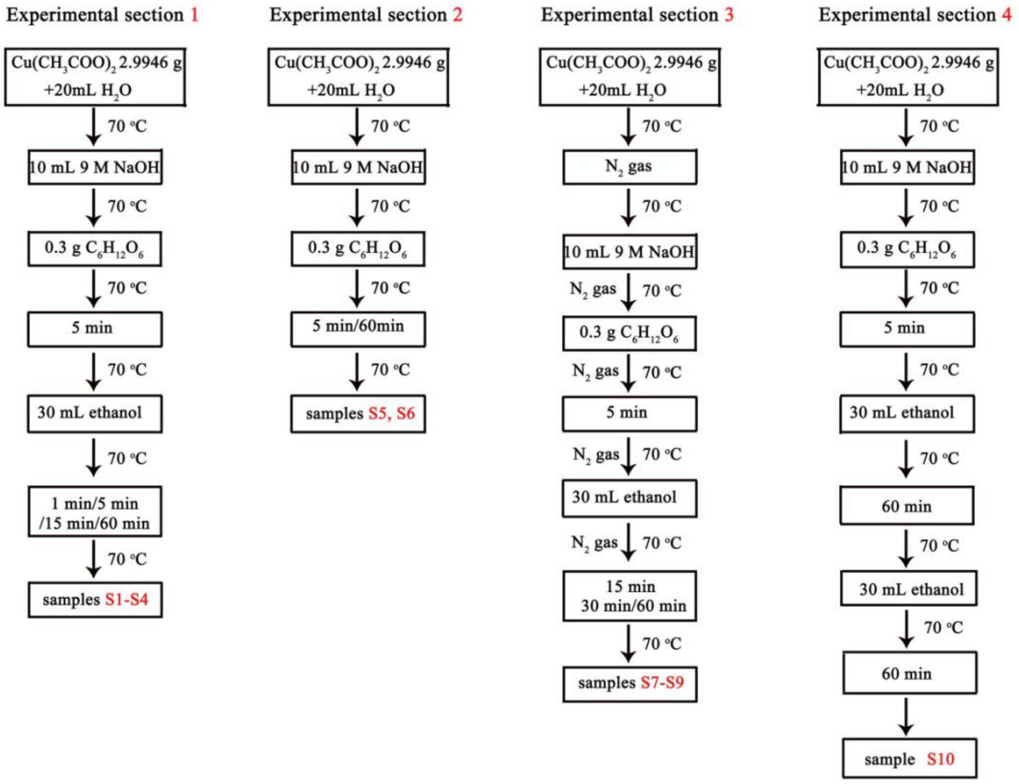
Experimental Section 3

All chemicals used in our experiment were of analytical grade and used without further purification. In a typical experiment, $Cu(CH_3COO)_2$ (2.9946 g) was dissolved in deionized water (20 mL) under a constant stirring at 70 °C for 2 min. Then N_2 gas was purged into the reaction system to remove dissolved O_2 during the whole reaction process. 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. Then ethanol (30 mL) was added, when the reaction temperature enhanced up to 70 °C again, we collected the products at 15 min, 30 min and 60 min, respectively. Afterward, the obtained particles (samples S7-S9) 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.

Experimental Section 4

In a typical experiment, $Cu(CH_3COO)_2$ (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. Then ethanol (30 mL) was added, when the reaction temperature enhanced up to 70 °C again, we obtained the products at 60 min. Afterward, another 30 mL ethanol was further added into the above reaction system, and the products were obtained at 60 min. The obtained particles (samples S10) 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.

Scheme S1. Sample denotations and their corresponding detailed experimental conditions.



Theoretical Calculation

The density functional theory (DFT) calculation was performed using Dmol3 code which developed by Delley[1-3]. Firstly, a Cu_2O crystal cell was optimized and then based on this cell, a 4 nm octahedral nanoparticle was built. Three ethanol molecules were put on the apex, edge and facet, respectively. The stuctures of each ethanol molecules were optimized and then their adsorption energies were seperately calculated using following equation:

$$E_{ad} = E_{total} - E_s - E_m \qquad (1)$$

where E_{total}, E_s and E_m are the bond energy of the whole system, Cu_2O part, and free ethanol molecules, respectively. Both the structure optimization and energy calculation 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 pseudopots (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^{-6} Hartree (2.72×10^{-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. B. Delley, An All-Electron Numerical-Method for Solving the Local Density Functional for Polyatomic-Molecules. *J Chem Phys*, 1990**, 92** (1), 508-517.

2. B. Delley, From molecules to solids with the DMol(3) approach. *J Chem Phys*, 2000**, 113** (18), 7756-7764.

3. B. Delley, DMol(3) DFT studies: from molecules and molecular environments to surfaces and solids. *Comp Mater Sci*, 2000**, 17** (2-4), 122-126.

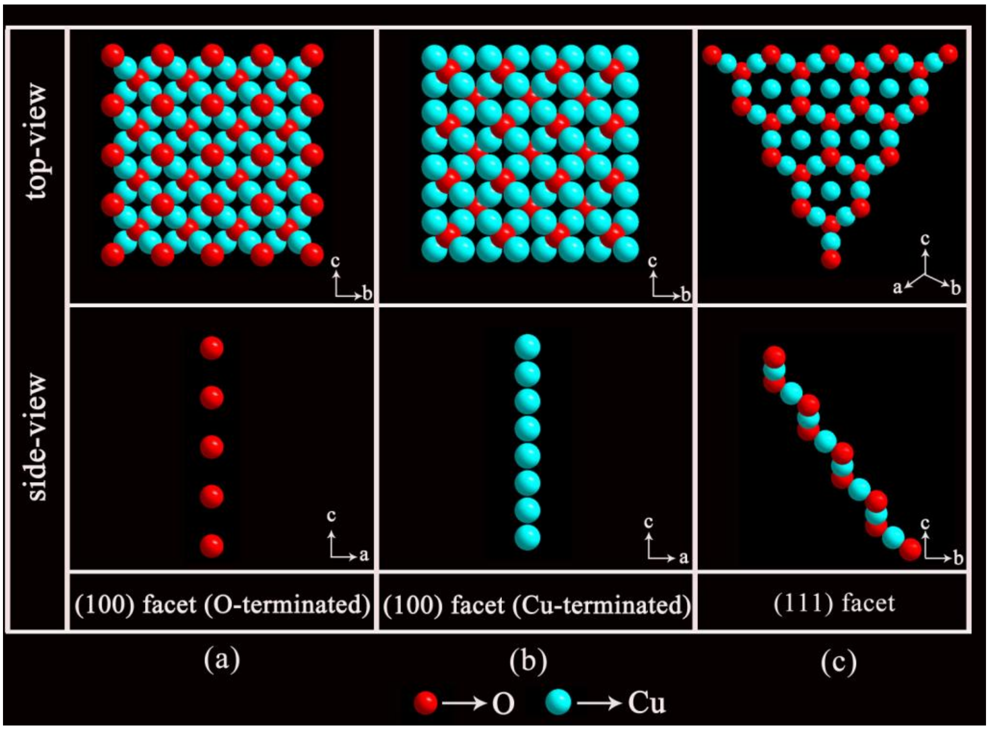


Fig. S1 The crystallographic structures of (100) (a and b) and (111) (c) facets of Cu_2O crystal.

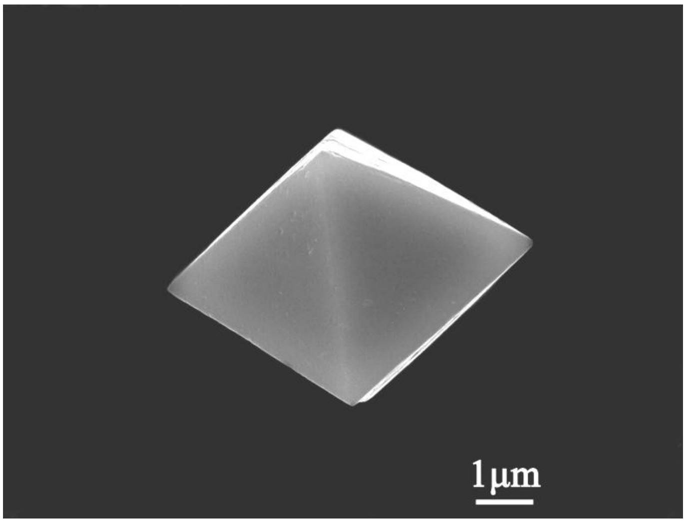


Fig. S2 FE-SEM image of a typical individual particle obtained in the absence of ethanol for 5 min (Experimental Section 2, sample S5).

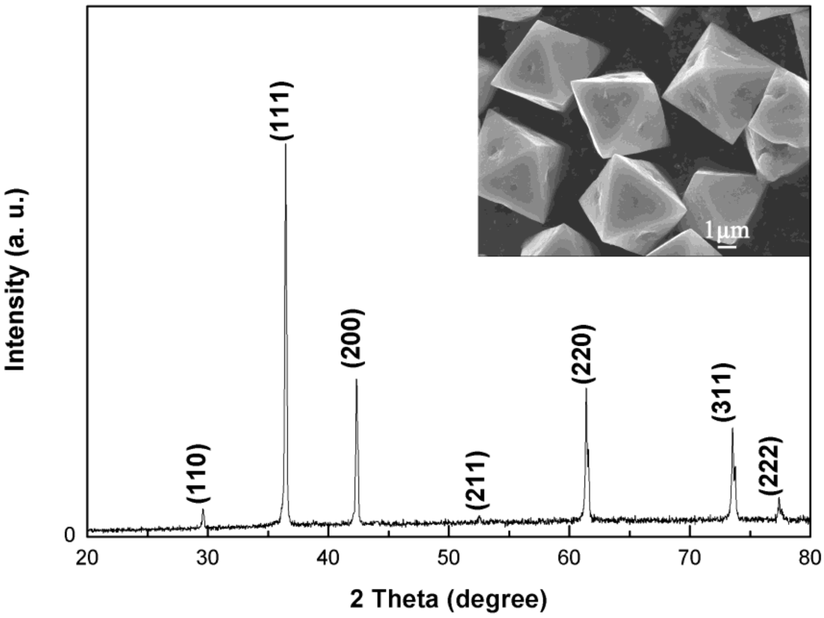


Fig. S3 XRD pattern of the typical hexapod-like Cu_2O architectures obtained at 60 min in the presence of ethanol, the insert is the corresponding low-magnification FESEM image (Experimental Section 1, sample S4).

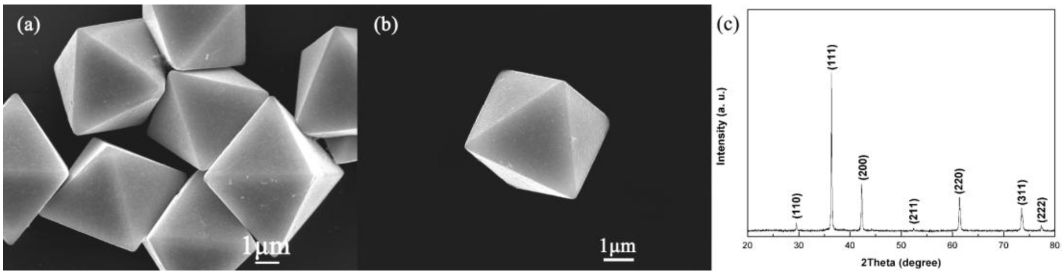


Fig. S4 FESEM images and XRD pattern of the typical Cu_2O crystals obtained at 60 min in the absence of ethanol (Experimental Section 2, sample S6). (a) Low magnification FESEM image, (b) FESEM image of a individual particle, (c) XRD pattern of the products.

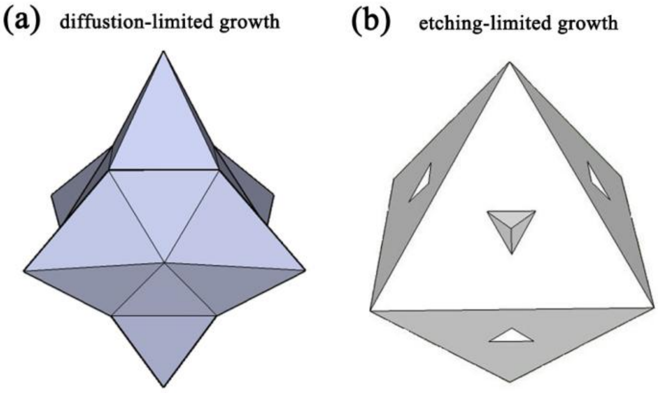


Fig. S5 Schematic illustrations of (a) diffusion-limited growth and (b) etching-limited growth.

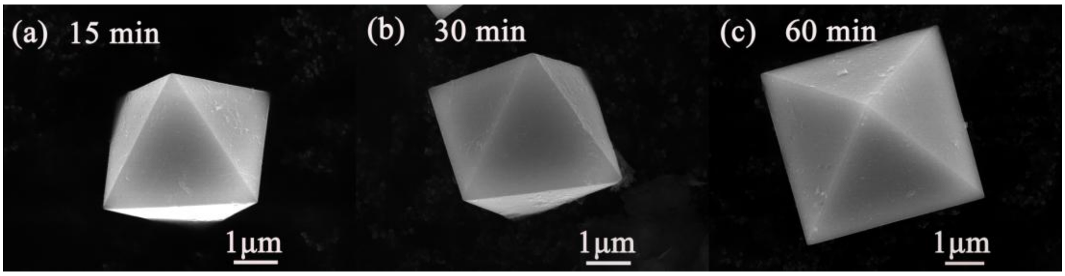


Fig. S6 FE-SEM images of the products obtained at different reaction time when N_2 gas was purged into the ethanol-water system to remove dissolved O_2 during the reaction (Experimental Section 3, samples S7-S9). It is seen that the product is still octahedral morphology with well-defined {111} facets, which indicates that the centers of {111} facets are not etched.

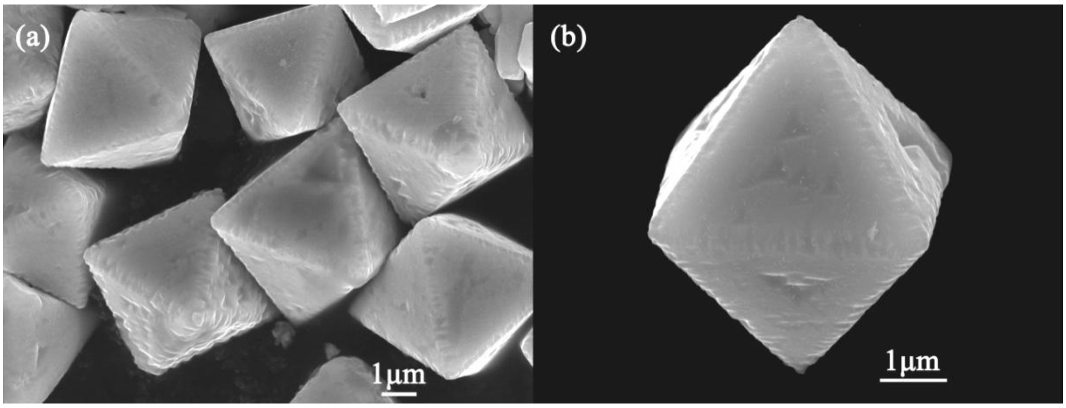


Fig. S7 FE-SEM images of the products obtained when another 30 mL ethanol was further added into the reaction system after 60 min (Experimental Section 4, sample S10). (a) Low magnification, (b) A individual particle. It can be seen that steps are formed on the edges and vertices, suggesting the presence of etching.

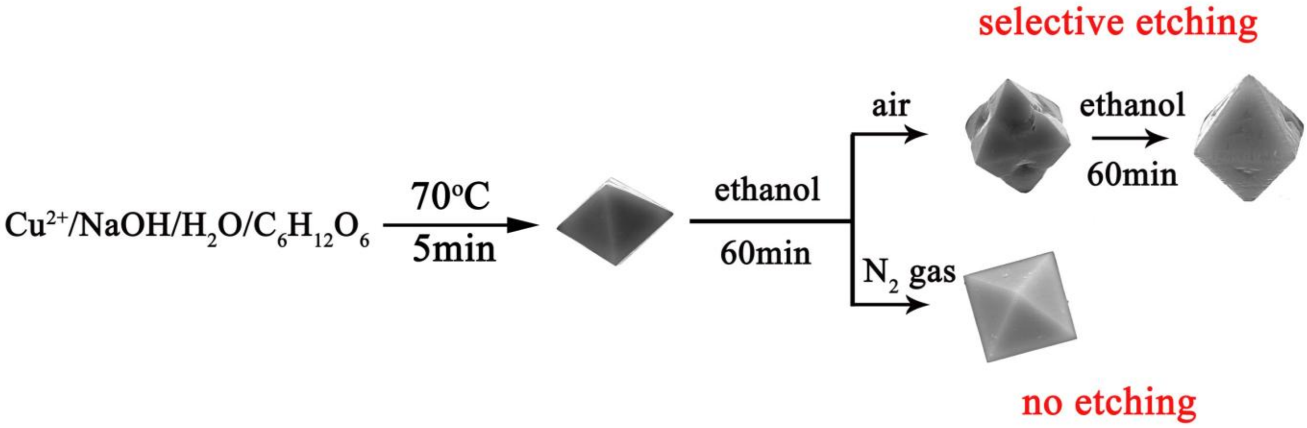


Fig. S8 A schematic illustration of the reaction pathways and shapes of the corresponding products by etching-limited branching growth.

The oxidative etching process can be described as the following reaction equation.[9]

$$2Cu_2O+O_2+4H_2O\rightarrow4Cu^{2+}+8OH^-$$

[9] Y. M. Sui, W. Y. Fu, Y. Zeng, H. B. Yang, Y. Y. Zhang, H. Chen, Y. G. Li, M. H. Li, G. T. Zou, *Angew. Chem., Int. Ed.*, 2010, **49**, 1.

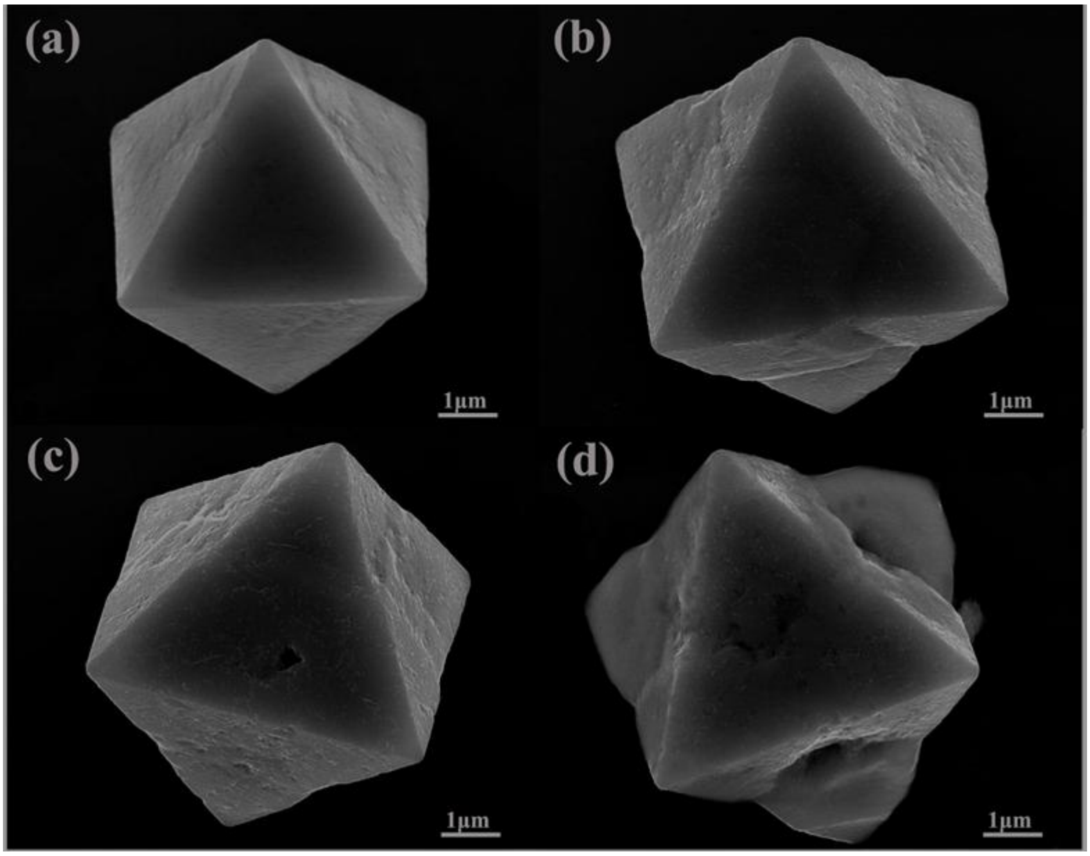


Fig. S9 FE-SEM images of the synthesized Cu_2O crystals dipped in ethanol solution (30ml ethanol and 30ml water) at 70℃ with different reaction time.(a)5min,(b)10min,(c)15min,(d)30min