Electronic Supplementary Information

Facet-Dependent Oxysulfidation of Cu_2O Nanomaterials: Implications for Improving the Efficacy of Nanopesticides

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Number of pages: 12

Number of tables: 3

Number of figures: 6

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S1. Chemicals.

Cupric chloride dihydrate ($CuCl_2 \cdot 2H_2O$), cupric sulfate ($CuSO_4$), polyvinylpyrrolidone (PVP, molecular weight = 30000), sodium hydroxide (NaOH), ascorbic acid, oleic acid, D-(+)-glucose, sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$), 4-hydroxyethylpiperazine-1-propanesulfonic acid (HEPPS), and 2,9-dimethyl-1,10-phenanthroline (neocuproine) were purchased from Aladdin Co. Ltd. Ethanol and cyclohexane were obtained from Tianjin Chemical Reagent Co. All chemicals were analytical grade and used without further purification. Deionized (DI) water was used in all experiments.

S2. Oxidation of Cu_2O nanomaterials.

The oxidation of Cu_2O nanomaterials with different exposed facets was investigated in batch tests. High-purity O_2 was purged into 20 mL of aqueous solution containing 50 mg of Cu_2O nanomaterials. After 9 h of reaction, the oxidized Cu_2O nanomaterials were collected by centrifugation at 13000 *g* for 15 min and allowed to dry in a vacuum-freezing dryer to obtain the solid materials for characterization by X-ray diffraction (XRD).

Table S1 Selected physicochemical properties of Cu_2O nanomaterials.

Samples	Shape	d [a] (nm)	Predominant exposed facet
Cu_2O_{100}	cube	887 ± 135	{100}
Cu_2O_{111}	octahedron	860 ± 97	{111}
Cu_2O_{110}	rhombic dodecahedron	509 ± 80	{110}

[a] d = edge length of single nanomaterials determined by counting 200 particles in SEM images.

Table S2 Sulfur to copper (S/Cu) ratio of oxysulfidized Cu_2O nanomaterials at reaction time of 1 day.

Samples	Atomic ratio of S/Cu [a]
Oxysulfidized Cu_2O_{100}	0.98
Oxysulfidized Cu_2O_{111}	0.96
Oxysulfidized Cu_2O_{110}	0.67

[a] Analyzed by energy dispersive X-ray spectroscopy (EDS) attached to the SEM.

Table S3 Crystalline phases identified in oxysulfidized Cu_2O nanomaterials at different reaction times.

Samples	Crystalline phases [a] (10 min)	Crystalline phases [a] (1 day)
Oxysulfidized Cu_2O_{100}	cuprite@yarrowite-covellite	covellite
Oxysulfidized Cu_2O_{111}	cuprite@yarrowite	covellite
Oxysulfidized Cu_2O_{110}	cuprite@djurleite	cuprite@covellite

[a] Analyzed by X-ray diffraction (XRD) and determined using MDI Jade 6 software, where cuprite corresponds to Cu_2O (JCPDS No. 05-0667), djurleite corresponds to $Cu_{31}S_{16}$ (JCPDS No. 34-0660), yarrowite corresponds to Cu_9S_8 (JCPDS No. 36-0379), and covellite corresponds to CuS (JCPDS No. 06-0464).

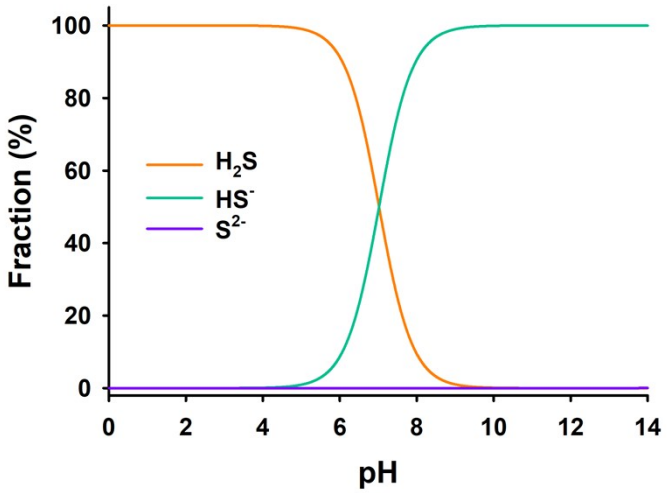

Fig. S1 Mass fractions of different sulfide species (H_2S, HS^-, and S^{2-}) in aqueous solution as a function of pH at 25 °C. Calculations are based on pK_{a1} = 7.02, pK_{a2} = 17.4.[1]

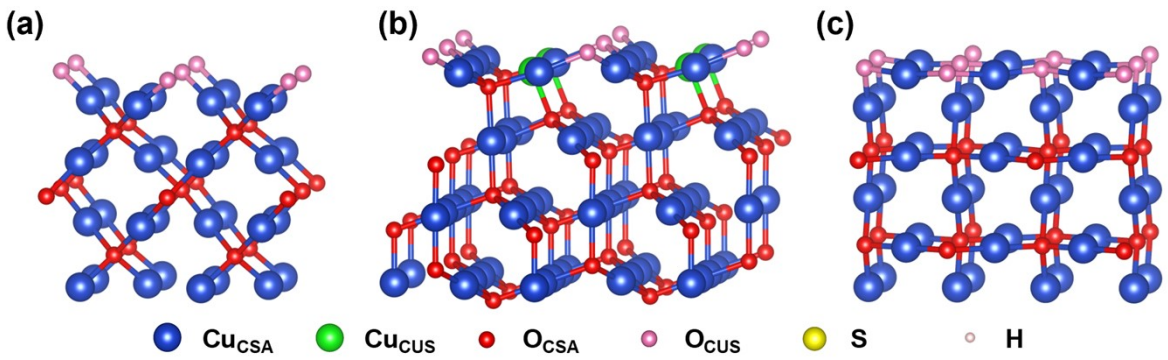

Fig. S2 Side views of optimized geometric structures (a-c) of Cu_2O nanomaterials: Cu_2O_{100} (a); Cu_2O_{111} (b); and Cu_2O_{110} (c).

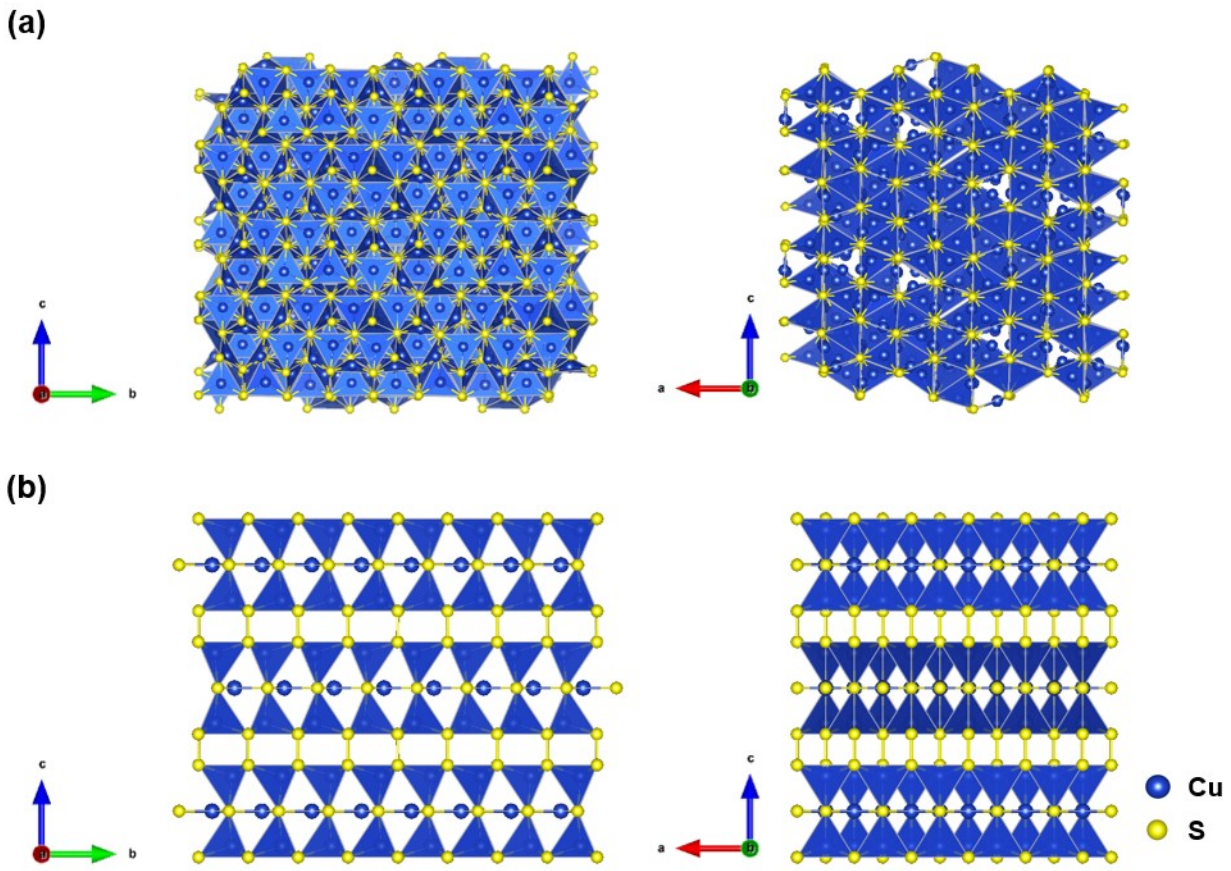

Fig. S3 Crystal structure of djurleite (a) and covellite (b) (data from American Mineral Crystal Structure Database, http://rruff.geo.arizona.edu/AMS/amcsd.php). The crystal structure of yarrowite is not displayed as it is still not determined.[2]

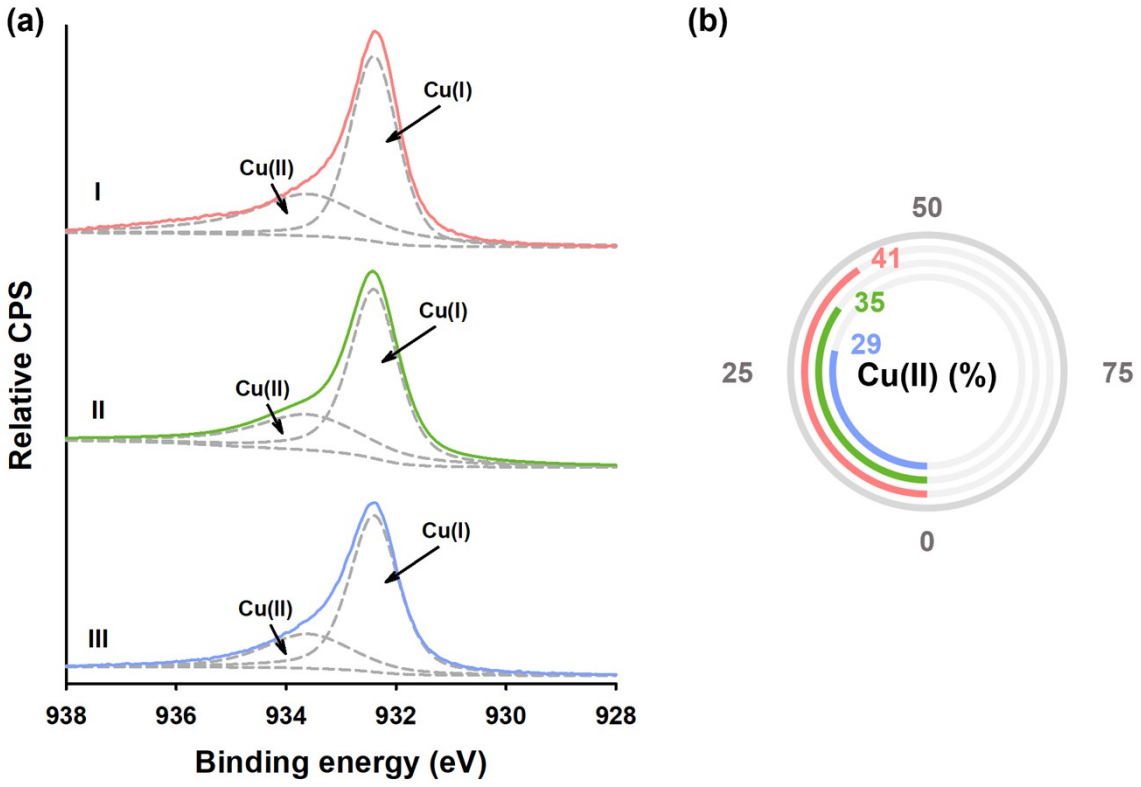

Fig. S4 Deconvoluted Cu 2p X-ray photoelectron spectroscopy (XPS) spectra (a) and the proportion of Cu(II) (b) of initial oxysulfidation products of Cu_2O nanomaterials after 10 min of reaction (I: oxysulfidized Cu_2O_{100}; II: oxysulfidized Cu_2O_{111}; III: oxysulfidized Cu_2O_{110}; these initial oxysulfidation products are represented by red, green, and blue colors in part b).

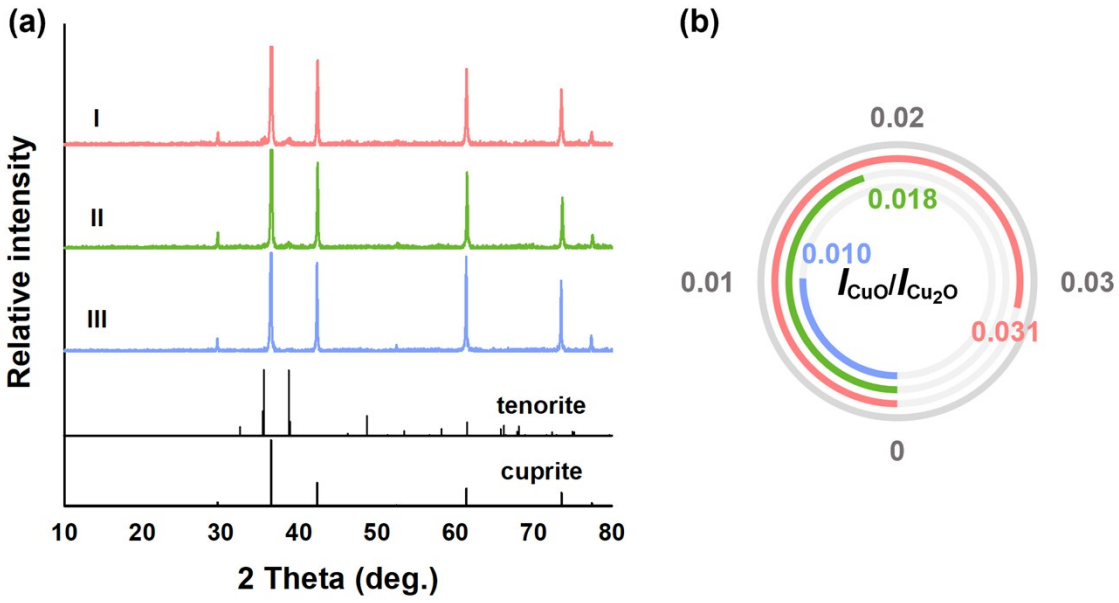

Fig. S5 XRD patterns of oxidized Cu_2O nanomaterials (a) and the ratio of the intensity of the highest peak of the CuO phase to that of the Cu_2O phase (b) (I: oxidized Cu_2O_{100}; II: oxidized Cu_2O_{111}; III: oxidized Cu_2O_{110}; these oxidized products are represented by red, green, and blue colors in part b).

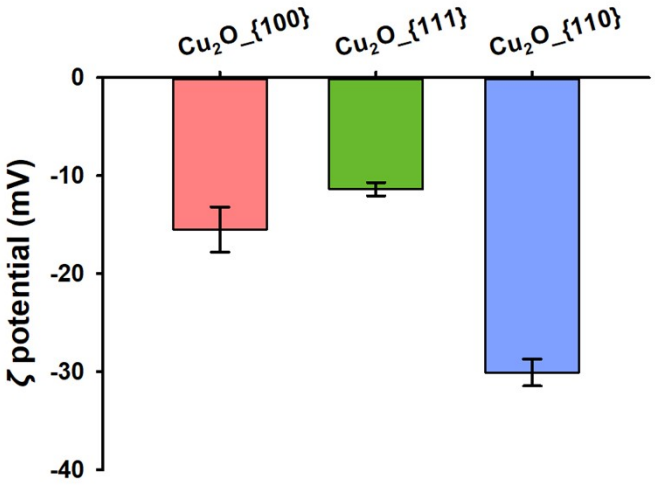

Fig. S6 ζ potential of Cu_2O nanomaterials in HEPPS buffer.

References

1. M. M. Benjamin, *Water Chemistry*, Waveland Press, Inc., 2014.

2. P. Roy and S. K. Srivastava, Nanostructured copper sulfides: Synthesis, properties and applications, *CrystEngComm*, 2015, **17**, 7801–7815.