

Supplementary Material (ESI) for RSC Advances

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Electronic Supplement for: Reduction of Cu₂O nanocrystals: reactant-dependent influence of capping ligands and coupling between adjacent crystal planes

Qing Hua, Kai Chen, Sujie Chang, Huizhi Bao, Yunsheng Ma, Zhiqian Jiang, Weixin Huang*

Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Materials for Energy Conversion and Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China.

E-mail: huangwx@ustc.edu.cn

Experimental Details

In this work, five types of Cu₂O nanocrystals were prepared. All the chemicals were analytical grade reagents and used as received without further purification.

The synthesis of cubic, octahedral and {100} truncated octahedral Cu₂O nanocrystals followed Zhang et al.'s recipe.¹ In a typical procedure, 5.0 mL NaOH aqueous solution (2.0 mol/L) was added dropwise into 50 mL CuCl₂ aqueous solution (0.01 mol/L) containing different amounts of PVP (MW = 30000) (cubic: 0 g; octahedral: 4.44 g; {100} truncated octahedral: 1.67 g) at 55 °C. After adequately stirring for 0.5 h, 5.0 mL ascorbic acid aqueous solution (0.6 mol/L) was added dropwise into the solution. The mixed solution was adequately stirred for different time (cubic: 5 h; octahedral: 3 h; {100} truncated octahedral: 3 h) at 55 °C. The resulting precipitate was collected by centrifugation and decanting, then washed with distilled water and absolute ethanol, and finally dried in vacuum at RT for 12 h. The synthesis of octahedral, rhombic dodecahedral and {110} truncated octahedral Cu₂O nanocrystals followed Liang et al.'s recipe.² In a typical procedure, 1 mmol CuSO₄ was dissolved in 40 mL water to form a clear solution into which different amounts of oleic acid (octahedral: 2.5 mL; rhombic dodecahedral: 4 mL; {110} truncated octahedral: 3.5 mL) and 20 mL absolute ethanol were added successively with vigorous stirring. When the mixture was heated to 100 °C, 10 mL NaOH solution (8 mmol) was added. After 5 min, 30 mL aqueous solution containing 3.42 g D-(+)-glucose was added

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under constant stirring. The mixture reacted for another 60 min and a brick-red color gradually appeared. The resulting precipitate was collected by centrifugation and decanting, then washed with distilled water and absolute ethanol, and finally dried in vacuum at RT for 12 h.

Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert PRO diffractometer using a nickel-filtered Cu K α (wavelength: 0.15418 nm) radiation source with the operation voltage and operation current being 40 kV and 40 mA, respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 high performance electron spectrometer using monochromatized Al K α ($h\nu$ = 1486.7 eV) as the excitation source. The likely charging of samples was corrected by setting the binding energy of the adventitious carbon (C 1s) to 284.8 eV. Scanning electron microscope (SEM) experiments were performed on a FEI Sirion200 field emission scanning electron microscope operated at beam energy of 5.0 kV.

The reducibility of Cu₂O nanocrystals was investigated by the temperature programmed reduction (TPR) technique employing H₂ (H₂-TPR) or CO (CO-TPR) as the reducing gas. Typically, 10 mg of catalyst was placed in a quartz reactor and heated at a rate of 5 °C /min. In H₂-TPR, 5% H₂ balanced with Ar with a flow rate of 20 mL/min was used and the consumption of H₂ was measured by a thermal conductivity detector (TCD). In CO-TPR, 1% CO balanced with Ar with a flow rate of 30 mL/min was used and the CO₂ product was online analyzed by a HIDEN QIC-20 gas analysis system. The reduction of Cu₂O nanocrystals by the adventitious carbon and capping ligands was also studied by means of temperature programmed reaction spectroscopy (TPRS) in which 10 mg of Cu₂O nanocrystals was heated in a quartz reactor in Ar (flow rate of 30 mL/min) at a heating rate of 5 °C /min and all likely products (CO₂, H₂O, H₂, CO, N₂, NH₃, NO, and NO₂) were online analyzed by a HIDEN QIC-20 gas analysis system.

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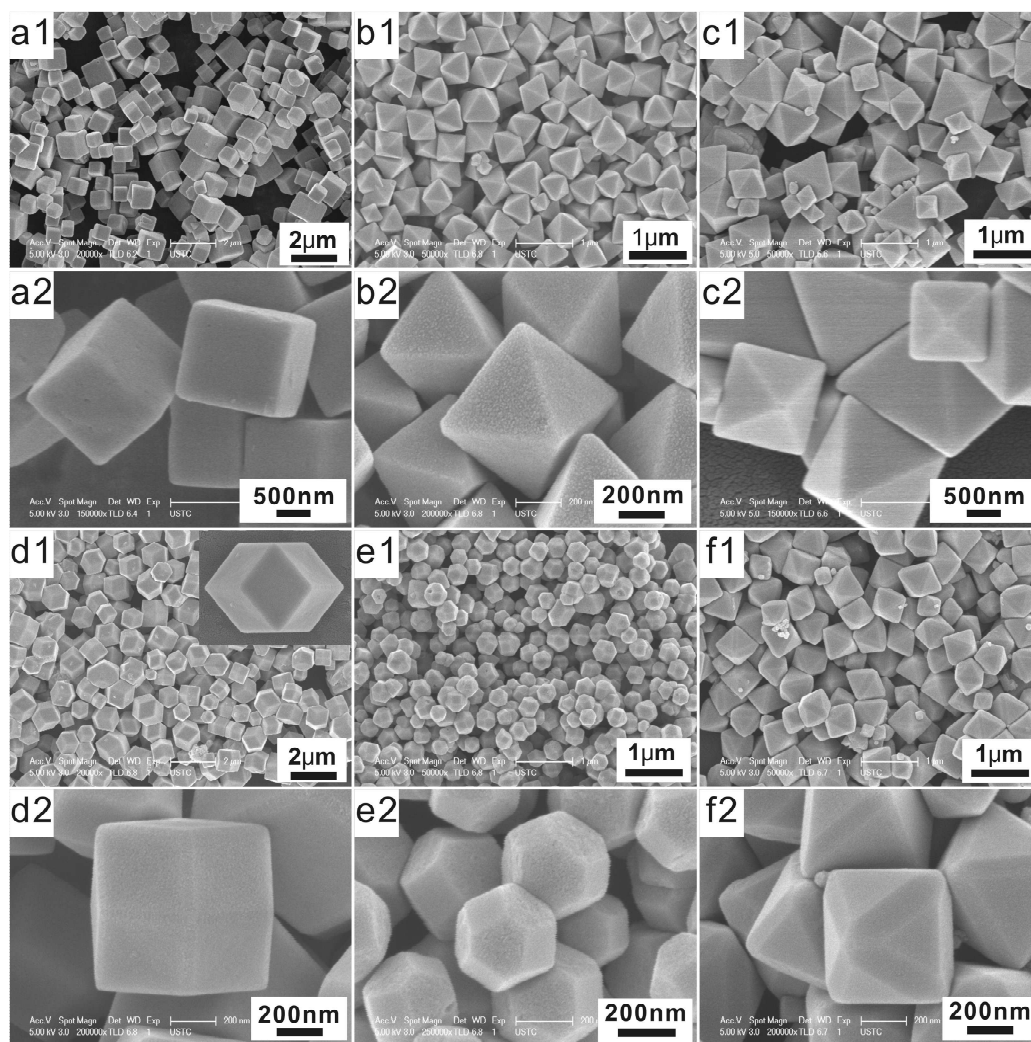


Fig. S1 SEM images of uniform Cu_2O nanocrystals with different shapes: (a1 & a2) cubes; (b1 & b2) octahedra capped with PVP; (c1 & c2) octahedra capped with oleic acid; (d1 & d2) rhombic dodecahedra capped with oleic acid; (e1 & e2) {100} truncated octahedra capped with PVP; (f1 & f2) {110} truncated octahedra capped with oleic acid.

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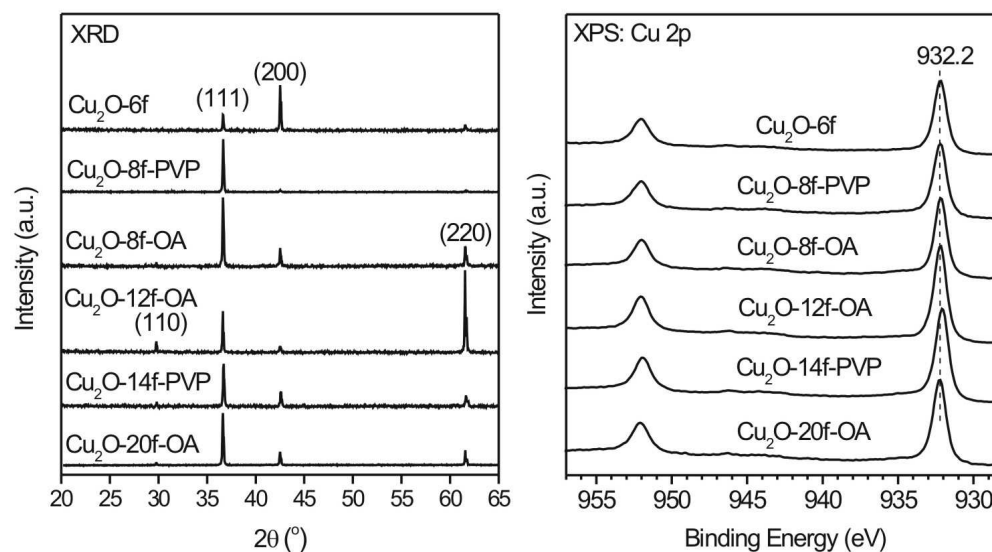


Fig. S2 XRD patterns and Cu 2p XPS spectra of Cu₂O cubes (Cu₂O-6f), Cu₂O octahedra capped with PVP (Cu₂O-8f-PVP), Cu₂O octahedra capped with oleic acid (Cu₂O-8f-OA), Cu₂O rhombic dodecahedra capped with oleic acid (Cu₂O-12f-OA), {100} truncated Cu₂O octahedra capped with PVP (Cu₂O-14f-PVP), and {110} truncated Cu₂O octahedra capped with oleic acid (Cu₂O-20f-OA).

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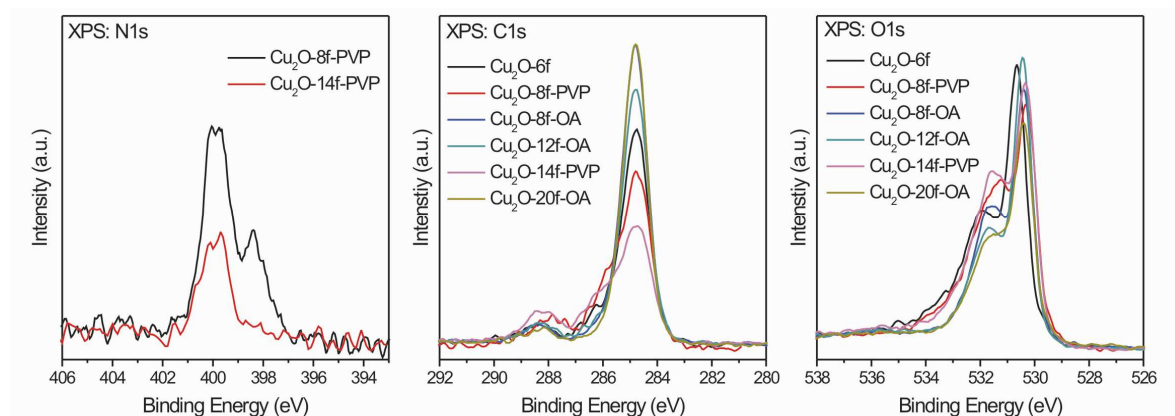


Fig. S3 N 1s, C 1s and O 1s XPS spectra of Cu_2O cubes ($\text{Cu}_2\text{O-6f}$), Cu_2O octahedra capped with PVP ($\text{Cu}_2\text{O-8f-PVP}$), Cu_2O octahedra capped with oleic acid ($\text{Cu}_2\text{O-8f-OA}$), Cu_2O rhombic dodecahedra capped with oleic acid ($\text{Cu}_2\text{O-12f-OA}$), {100} truncated Cu_2O octahedra capped with PVP ($\text{Cu}_2\text{O-14f-PVP}$), and {110} truncated Cu_2O octahedra capped with oleic acid ($\text{Cu}_2\text{O-20f-OA}$).

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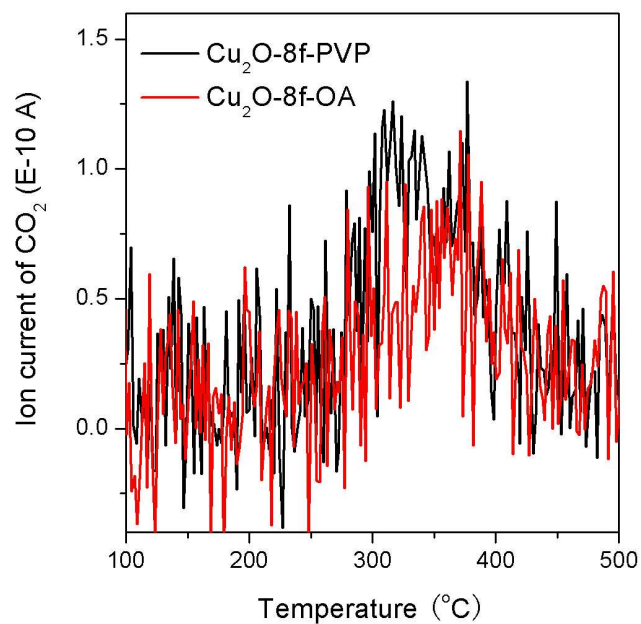


Fig. S4 The CO₂-TPRS spectra of Cu₂O octahedra capped with PVP (Cu₂O-8f-PVP) and Cu₂O octahedra capped with oleic acid (Cu₂O-8f-OA) in Ar.

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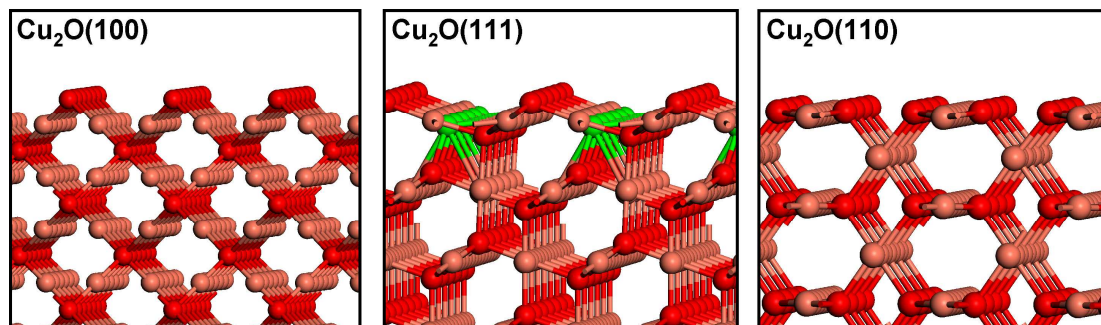


Fig. S5 Optimized structures of Cu_2O (100), (111) and (110) surfaces. The red, brick red and green balls represent oxygen, coordinated saturated copper (Cu_{CSA}) and coordinated unsaturated copper (Cu_{CUS}) atoms, respectively. On Cu_2O (100), the first layer consists of coordinated unsaturated O (O_{CUS}) and the second layer consists of coordinated saturated Cu (Cu_{CSA}). On $\text{Cu}_2\text{O}(111)$, the first layer consists of O (O_{CUS}), the second layer consists of Cu_{CSA} and coordinated unsaturated Cu (Cu_{CUS}) with a distance along z direction of 0.23 Å. On $\text{Cu}_2\text{O}(110)$, the first layer consists of both O_{CUS} and Cu_{CSA} and the second layer consists of Cu_{CSA} .

References

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- 2 X. D. Liang, L. Gao, S. W. Yang, J. Sun, *Adv. Mater.* 2009, **21**, 2068.