

Crystal Facet-Dependent Reactivity of Cu₂O in Direct Synthesis of Tetraethoxysilane from Silicon and Ethanol

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S1. Experimental Section

S1.1. Chemicals

Silicon powder (industrial grade) obtained from Hubei Xingfa Chemical Group Co., LTD. The particle size was approximately 150 μ m, the specific composition was analyzed by X-ray Fluorescence Spectrometer (XRF, PANalytical Axios) and shown in Table S1. Anhydrous ethanol (99.7%) was redistilled before use, dried and stored with 3A molecular sieve. NH_4F , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, NaOH , Ascorbic acid (AA), Polyvinylpyrrolidone (PVP, Mn=29000) and Triethoxysilane (TES) were both purchased from Sinopharm Chemical Reagent Co. Ltd.).

S1.2. Instrumentation

X-Ray powder diffraction (XRD, D/MAX, 2500V/PC) and fourier transform infrared spectroscopy (FT-IR, Nicolet iS 10) were used for the structural determination, further microstructural analyses were performed using field-emission scanning electron microscopy (FESEM, Hitachi-S4800 with an accelerating voltage of 20 kV) and transmission electron microscopy (TEM, JEOL JEM-2100F with an accelerating voltage of 200 kV). The surface element composition and chemical valence were identified by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD Kratos AXIS SUPRA). And the redox properties were explored by Temperature-programed reduction of H_2 (H_2 -TPR, AutoChem1 II 2920). Raman spectroscopic (Raman, Thermo Fischer DXR) and Electron Paramagnetic Resonance (EPR, Bruker EMXplus-6/1) were carried out to investigate the role of oxygen vacancy. All volatile products were characterized by gas chromatography-mass spectrometry (GC-MS, Agilent 7890A GC-5975C MS). The yield of products was determined by gas chromatography (GC, Agilent 7890B).

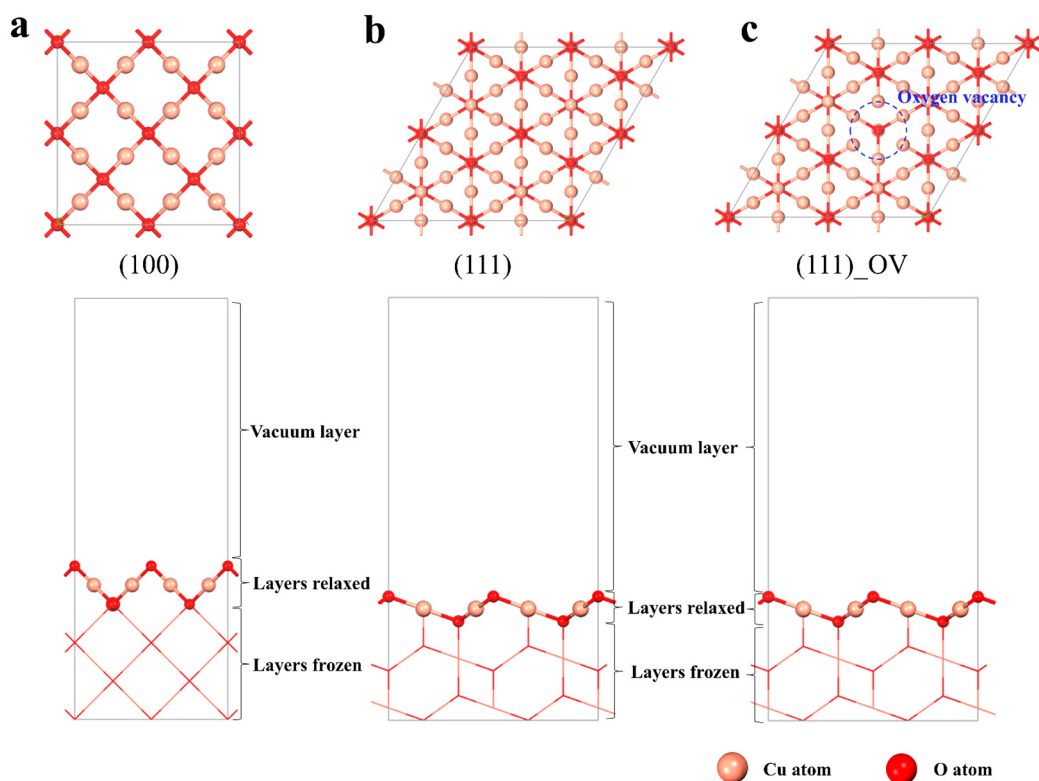


Figure S1. Top view and side view for different models: (a) Cu_2O (100), (b) Cu_2O (111), and (c) Cu_2O (111)_{OV} slab. The red and pink balls represent oxygen and copper atoms, respectively.

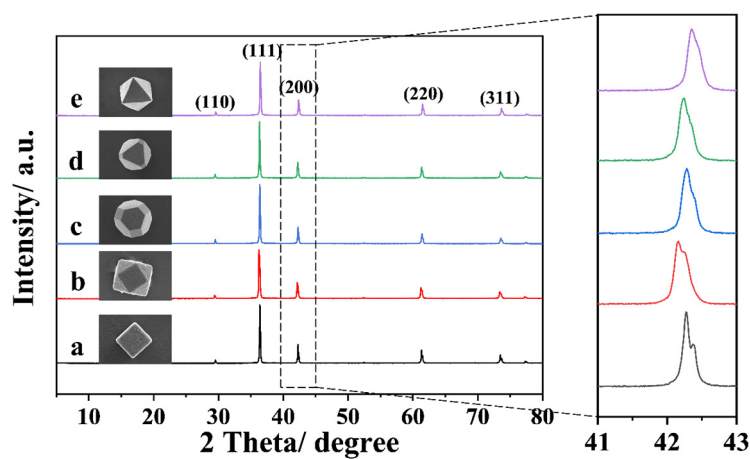


Figure S2. XRD patterns of Cu_2O crystals with different geometries, (a) cubes, (b) truncated cubes, (c,d) vertex-truncated octahedrons, (e) octahedrons. The left part is the standard XRD data of bulk Cu_2O . The left part shows the enlarged image of (200) peaks, it can be concluded that the intensity ratio of (111)/(200) increased as the shape of the products evolved from cubes through truncated cubes, vertex-truncated octahedrons and finally to octahedrons.

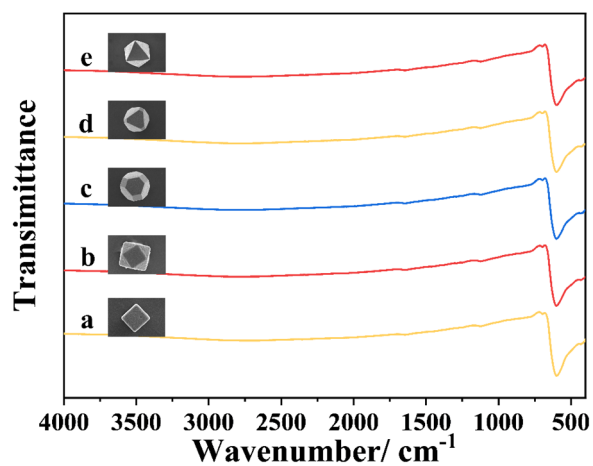


Figure S3. FTIR spectroscopy of Cu₂O crystals with different geometries, (a) cubes, (b) truncated cubes, (c,d) vertex-truncated octahedrons, (e) octahedrons.

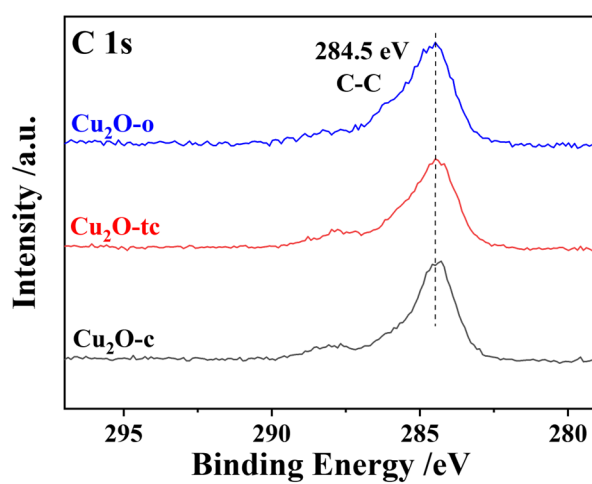


Figure S4. XPS spectra with C 1s of Cu₂O with different morphologies.

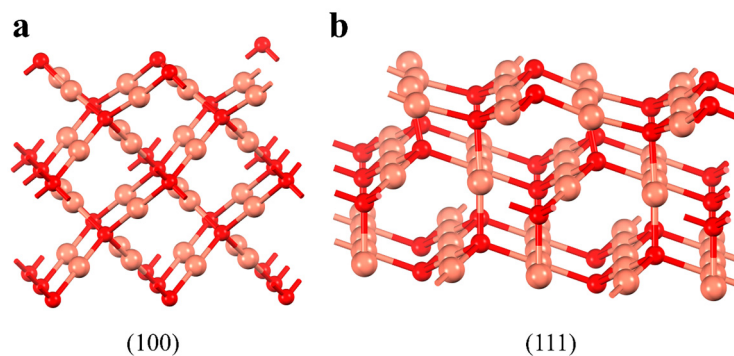


Figure S5. Optimized structures of Cu_2O (100) and (111) surfaces: (a) side view of the Cu_2O (100) surface, (b) side view of the Cu_2O (111) surface.

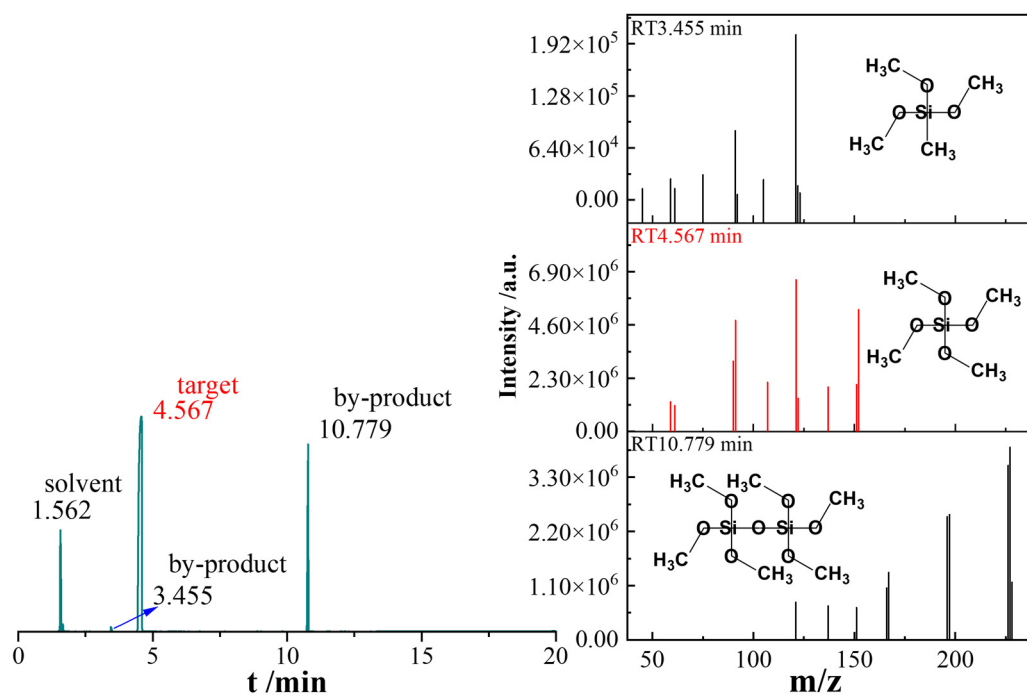


Figure S6. Total ion chromatogram and mass spectra of TMOS under different retention time.

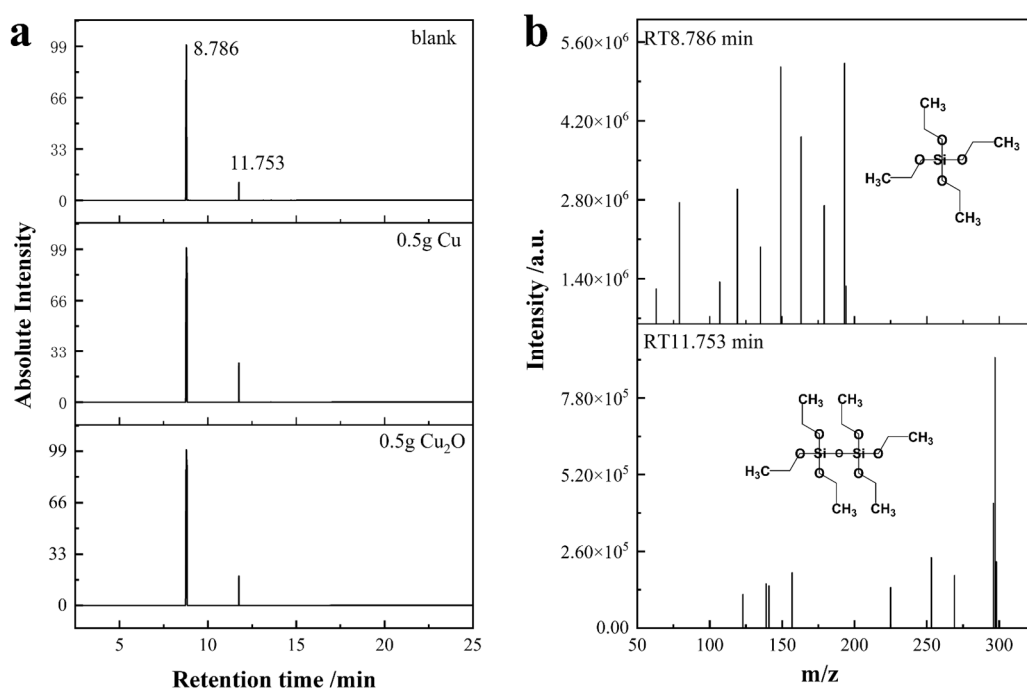


Figure S7. (a) Total ion chromatogram of products under different additive conditions, (b) mass spectra under different retention time.

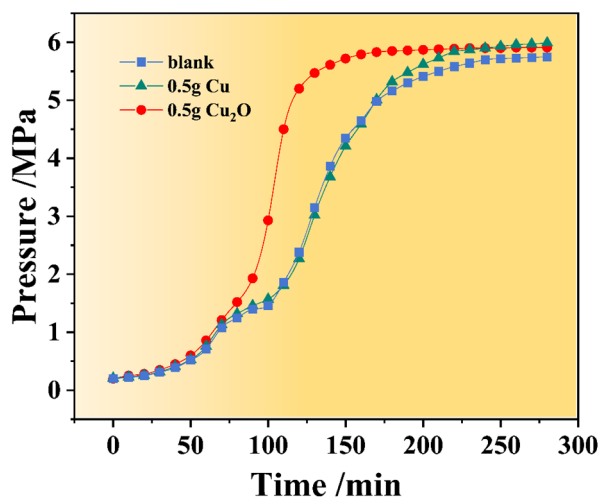


Figure S8. The variation of pressure in the high-pressure reactor over time under different additive conditions.

Table S1. The XRF of silicon powder.

	Si	Al	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zr
wt. %	99.43	0.050	0.0605	0.033	0.019	0.004	0.379	0.0130	0.005	0.0037

Table S2. O 1s results of Cu₂O with different morphologies.

Sample	O_{ads}	O_{latt}	O_{ads}/O_{latt}
Cu ₂ O-c	1.04066	1.04755	0.9934
Cu ₂ O-tc	0.57227	0.57617	0.9932
Cu ₂ O-o	0.10973	0.12339	0.8893

Table S3. Effect of reaction time and temperature on silicon conversion and TEOS yield.

Entry	Temperature (h)	Reaction Time (h)	Conversion Rate ^a	Yield ^b
1	160 °C	1	16.7%	12.4%
2	180 °C	1	42.1%	39.2%
3	200 °C	1	99.9%	92.5%
4	220 °C	1	99.9%	92.6%
5	200 °C	0.1	65.1%	59.3%
6	200 °C	0.5	95.4%	88.6%
7	200 °C	3	99.9%	91.7%

^a Conversion rate based on Si_{met}. ^b Yield of major product: TEOS.