

Electronic Supplementary Information for

**CuO Hollow Nanostructures Catalyzed [3+2] Cycloaddition of Azides with
Terminal Alkynes**

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I. Experimental

Preparation of Cu₂O nanocubes

PVP (Aldrich, Mw 55,000; 5.3 g) dissolved in 45mL of PD (Aldrich, 96%) was heated to 240 °C under inert conditions. Then, 4.0 mmol of Cu(acac)₂ (STREM, 98%) dissolved in 15mL of PD was injected into the hot PVP solution at 240 °C, and the mixture was stirred for 15 min at the same temperature. The colloidal dispersion was cooled to room temperature, and the product was separated by adding 150mL of acetone with centrifugation at 8000 rpm for 20 min. The precipitates were washed with ethanol several times, and re-dispersed in 50mL of ethanol.

Synthesis of CuO Hollow and Branched Nanostructures

An appropriate concentration of aqueous ammonia solution was added into 25mL of the Cu₂O cube dispersion in ethanol (16mM with respect to the precursor concentration). The mixture was subjected to stirring at room temperature for 2 h. The volume and concentration of the aqueous ammonia solution used for each structure were 1.0mL and 14.7 M for hollow cubes, 2.0mL and 7.36 M for hollow spheres, and 6.0mL and 2.45 M for urchin-like particles, respectively. For shape optimization of the hollow spheres, a 3.68 M aqueous ammonia solution was used. After the reaction, the products were collected by centrifugation at 6000 rpm for 20 min. For the mechanism study, the appropriate amount of NaOH (Aldrich, 99.998%) was dissolved in 1.0mL of aqueous ammonia solution (14.7 M). The resulting mixture was added to 25mL of the ethanol dispersion of Cu₂O cubes (16mM with respect to the precursor concentration), and was allowed to stir at room temperature for 2 h. Hollow cubes were obtained without NaOH. Addition of 20mg (0.50 mmol) and 50mg (1.3 mmol) of NaOH yielded hollow spheres and urchin-like particles, respectively.

General procedure for [3+2] Cycloaddition of Azides with Terminal Alkynes

In a 10 mL pressure tube schlenk, 4 mg of CuO hollow nanostructures, benzyl azide (0.13 mL, 1 mmol), phenylacetylene (0.17 mL, 1.5 mmol) and 2.4mL H₂O/*t*-BuOH (1.6 mL:0.8 mL) were added. The reaction mixture was stirred at 25°C. After three hours, the reaction mixture was poured into saturated 20 ml aqueous NH₄Cl solution. The product was extracted three times with 20 ml dichloromethane and dried using MgSO₄. The CuO hollow nanostructures was recovered by centrifugation and clean solution was analyzed by 300MHz NMR.

II. Characterization

The nanoparticles were characterized by TEM (Omega EM912 operated at 120 kV, Korea Basic Science Institute), HRTEM (Philips F20 Tecnai operated at 200 kV, KAIST), and ED (attached to EM912). Samples were prepared by putting a few drops of the corresponding colloidal solutions on carbon coated copper grids (Ted Pellar, Inc). X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/MAX-RB(12 kW) diffractometer. Nitrogen sorption isotherms were measured at 77 K with a BELSORP mini-II (BEL Japan Inc.). Before measurements, the samples were degassed in a vacuum at 150 °C for 6 h. The copper loading amounts were measured by MiniPal 2 energy dispersive X-ray fluorescence (EDXRF) spectrometer. The reaction products were analyzed by ¹H NMR using Varian Mercury Plus (300 MHz). Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants in Hertz.

Data for ¹H-NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz), and integration. All compounds 3a,⁽¹⁾ 3b,⁽¹⁾ 3c,⁽²⁾ 3d,⁽¹⁾ 3e,^{(3),(2)} 3f,⁽¹⁾ 3g,⁽²⁾ 3h,^{(4),(6)} 3i,⁽¹⁾ and 3j⁽⁵⁾ were known compounds.

1-Benzyl-4-phenyl-1H-1,2,3-triazole (3a): ¹H-NMR (CDCl₃, 300 MHz): δ = 7.81 (d, *J* = 7.2 Hz, 2H), 7.67 (s, 1H), 7.41-7.21 (m, 8H), 5.59 (s, 2H). ¹³C-NMR (CDCl₃, 75 MHz): δ = 147.6, 134.1, 129.9, 128.5, 127.5, 125.1, 118.9, 53.6.

1-Benzyl-4-(4-bromophenyl)-1H-1,2,3-triazole (3b): ¹H-NMR (CDCl₃, 300 MHz): δ = 7.74-7.66 (m, 5H), 7.62-7.57 (m, 4H), 7.55 (s, 1H), 5.23 (s, 2H). ¹³C-NMR (CDCl₃, 75

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MHz): δ = 147.1, 134.9, 134.0, 129.4, 129.0, 128.2, 126.1, 119.4, 54.2.

1-benzyl-4-(phenoxymethyl)-1H-1,2,3-triazole (3c): $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 7.51 (s, 1H), 7.30-7.21 (m, 8H), 6.95-6.92 (m, 2H), 5.46 (s, 2H), 5.13 (s, 2H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 158.0, 134.3, 129.3, 128.9, 128.6, 127.9, 121.0, 114.6, 62.0, 54.2.

(1-Benzyl-1H-1,2,3-triazol-4-yl)methanol (3d): $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 7.47 (s, 1H), 7.29-7.25 (m, 3H), 7.21-7.18 (m, 2H), 5.40 (s, 2H), 4.86 (s, 1H), 4.65 (s, 2H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 148.5, 134.8, 129.2, 128.8, 128.2, 122.3, 55.9, 54.3.

(1-benzyl-1H-1,2,3-triazol-4-yl)(phenyl)methanol (3e): $^1\text{H-NMR}$ (DMSO , 300 MHz): δ = 7.94 (s, 1H), 7.43-7.34 (m, 3H), 7.33-7.29 (m, 5H), 7.26-7.22 (m, 2H), 6.02 (d, J = 4.8 Hz, 1H), 5.84 (d, J = 4.2 Hz, 1H), 5.54 (s, 2H). $^{13}\text{C-NMR}$ ($(\text{CD}_3)_2\text{SO}$, 75 MHz): δ = 152, 142, 136.7, 129.4, 128.7, 127.7, 124.4, 71.3, 53.4.

Ethyl-1-benzyl-1H-1,2,3-triazole-4-carboxylate (3f): $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 7.85 (s, 1H), 7.28-7.14 (m, 5H), 5.46 (s, 2H), 4.27 (q, J = 7.4 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 160.1, 140.7, 133.1, 128.7, 127.9, 127.6, 60.7, 53.9, 13.7.

Methyl 1-benzyl-1H-1,2,3-triazole-carboxylate (3g): $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 7.97 (s, 1H), 7.34-7.31 (m, 3H), 7.23-7.18 (m, 2H), 5.54 (s, 2H), 3.84 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 133.6, 129.6, 129.4, 128.5, 127.3, 54.7, 52.2.

1-benzyl-4-trimethylsilanyl-1H-1,2,3-triazole(3h): $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 7.54 (s, 1H), 7.35-7.22 (m, 5H), 5.53 (s, 2H), 0.29 (s, 9H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 148.2, 136.17, 130.2, 129.8, 129.4, 129.2, 54.5.

1,4-Diphenyl-1H-1,2,3-triazole (3i): $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 8.20 (s, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 7.56 (t, J = 7.65 Hz, 2H), 7.48-7.44 (m, 3H), 7.40-7.34 (m, 1H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 133.7, 129.2, 128.6, 127.0, 126.1, 125.3, 119.9, 117.7.

1-(4-Methoxybenzyl)-4-phenyl-1H-1,2,3-triazole (3j): $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 8.10 (s, 1H), 7.90 (dd, J = 7.7, 1.5 Hz, 2H), 7.67 (dd, J = 8.0, 1.5 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 6.6 Hz, 1H), 7.02 (dt, J = 9 Hz, 2H), 3.86 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 160.1, 148.4, 130.6, 129.1, 128.5, 126.0, 122.4, 120.2, 118.1, 115.3, 115.0, 55.8.

III. Figures

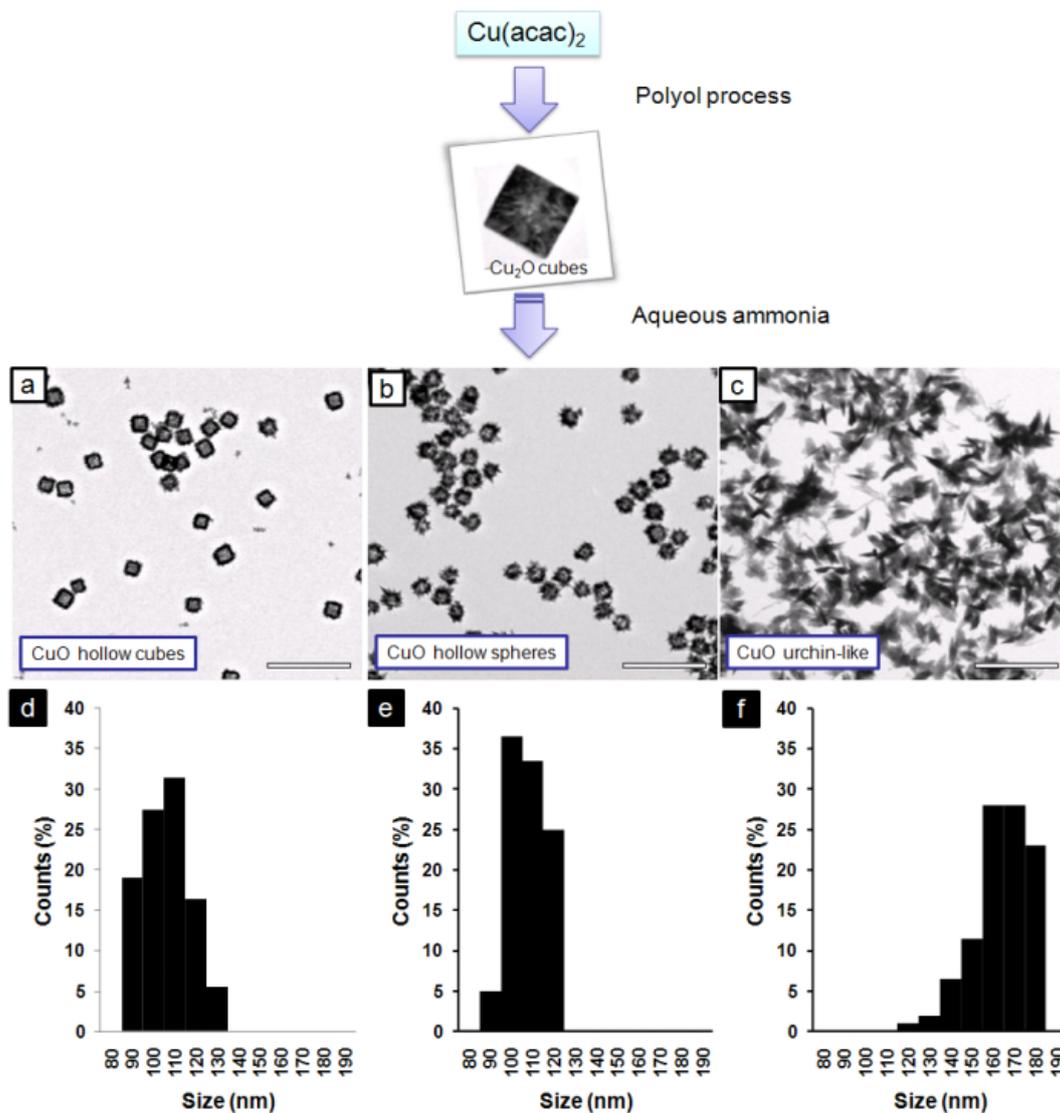


Figure S1. Overall synthetic scheme of various CuO nanostructures. TEM images and their size distribution diagrams for the CuO hollow cubes (a, d), hollow spheres (b, e) urchin-like particles (c, f). The scale bars represent 500 nm.

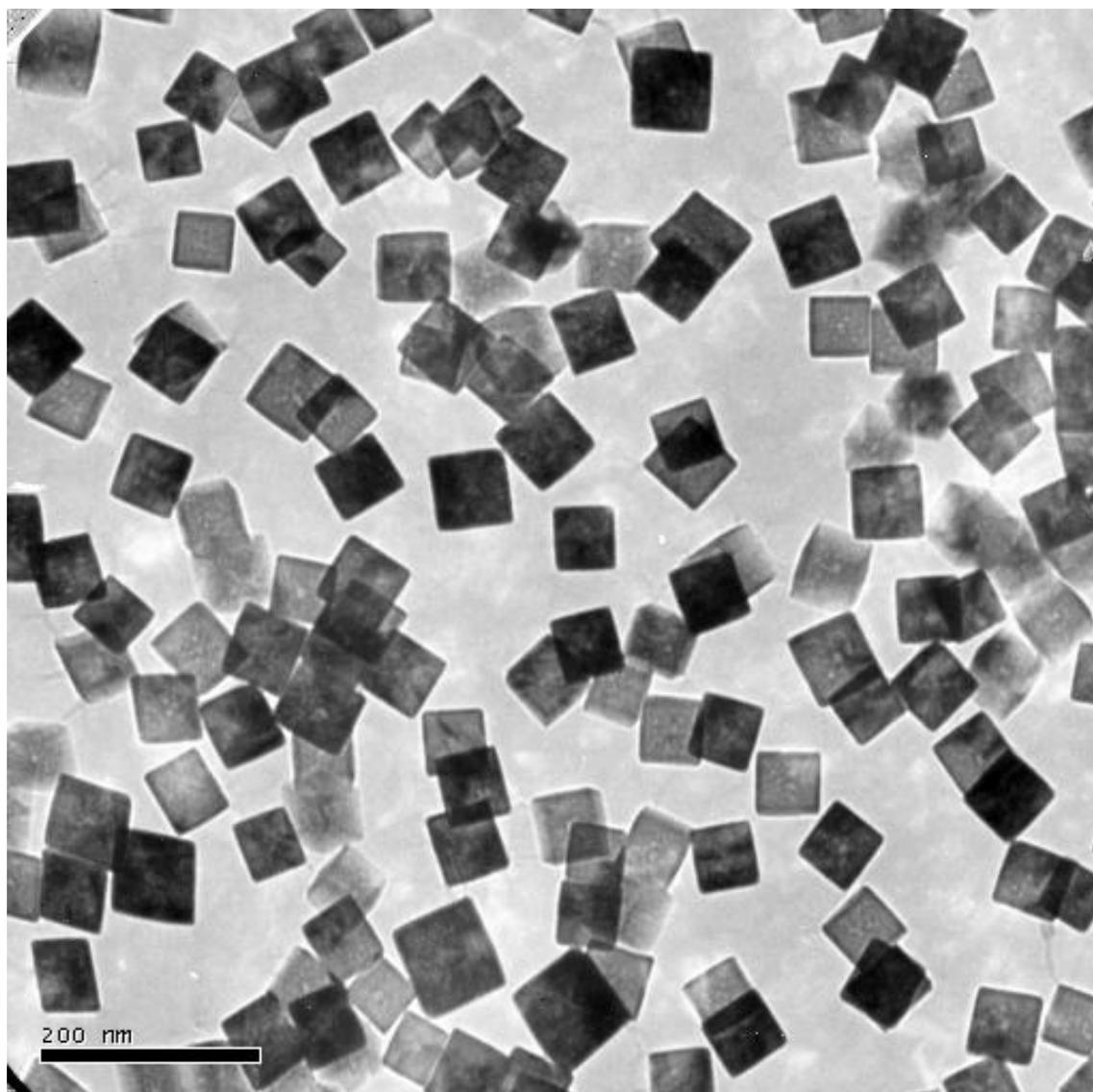


Figure S2. Magnified TEM images of Cu₂O nanocubes in Fig. 1

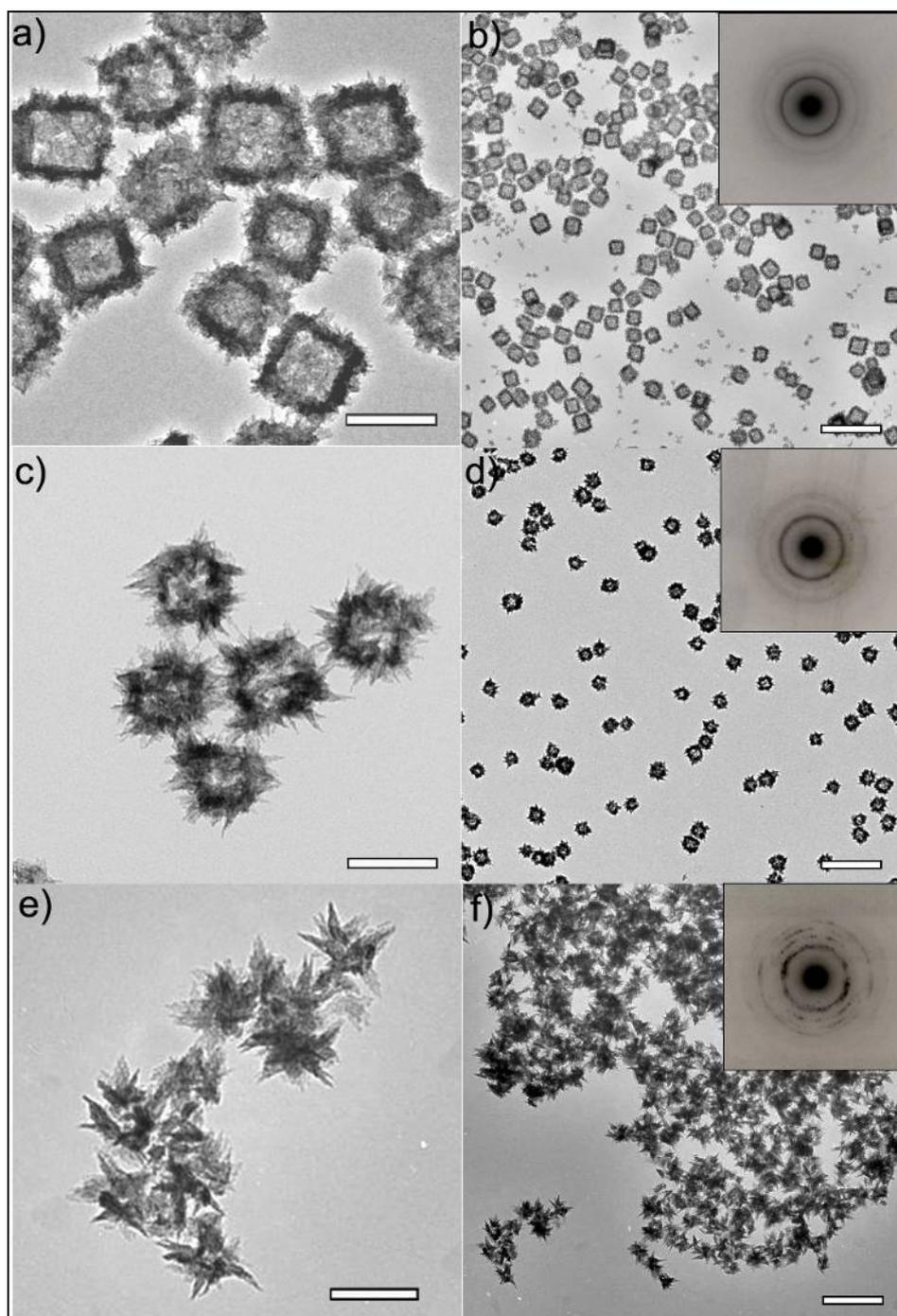


Figure S3. TEM images of CuO hollow cubes (a, b), hollow urchins (c, d), and urchins (e, f). The insets represent their SAED pattern of single particle, respectively. The bars represent 100 nm (a, c), 200 nm (e) and 500nm (b, d, e), respectively.

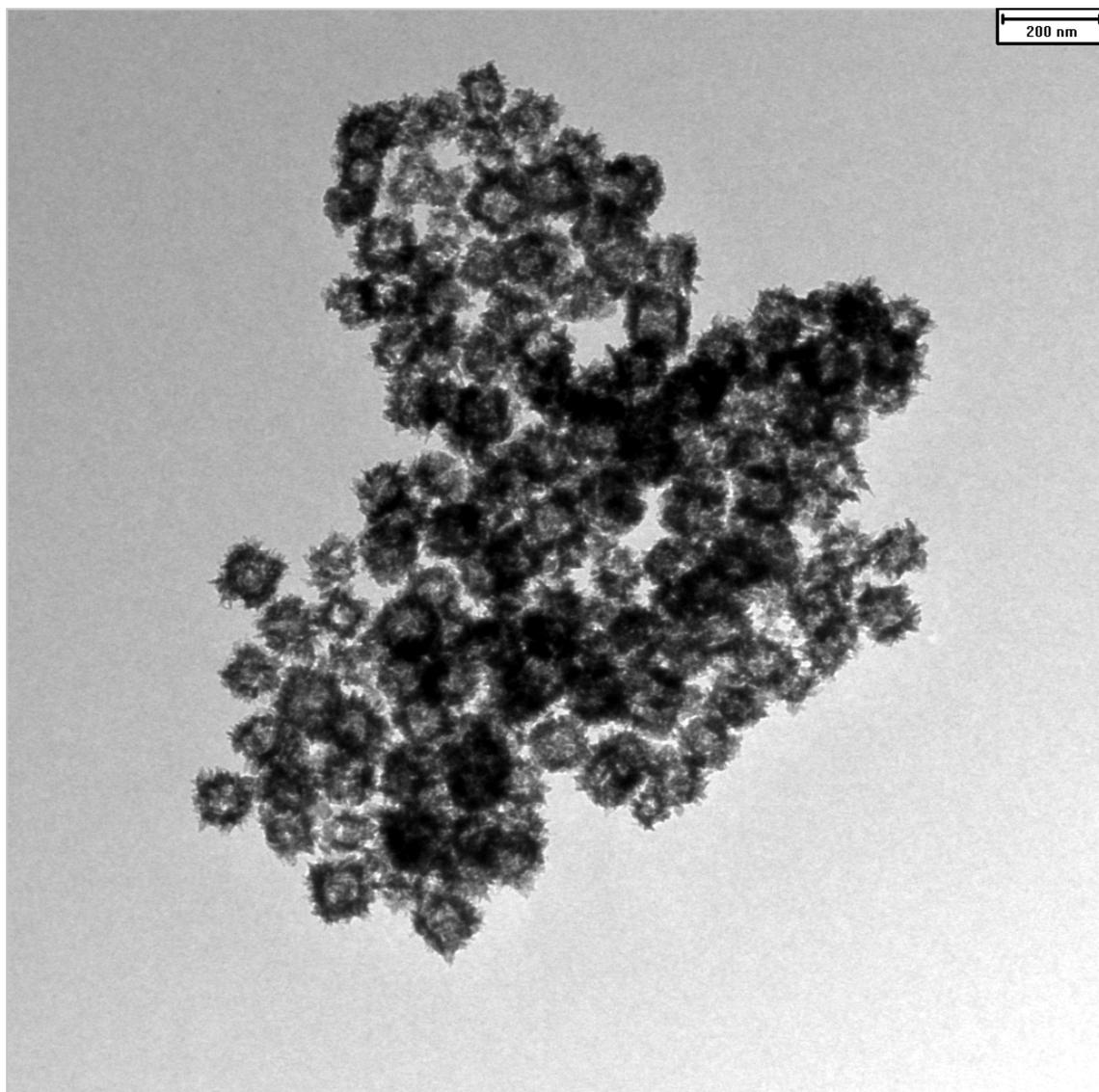


Figure S4. Magnified TEM images in Fig.2b.

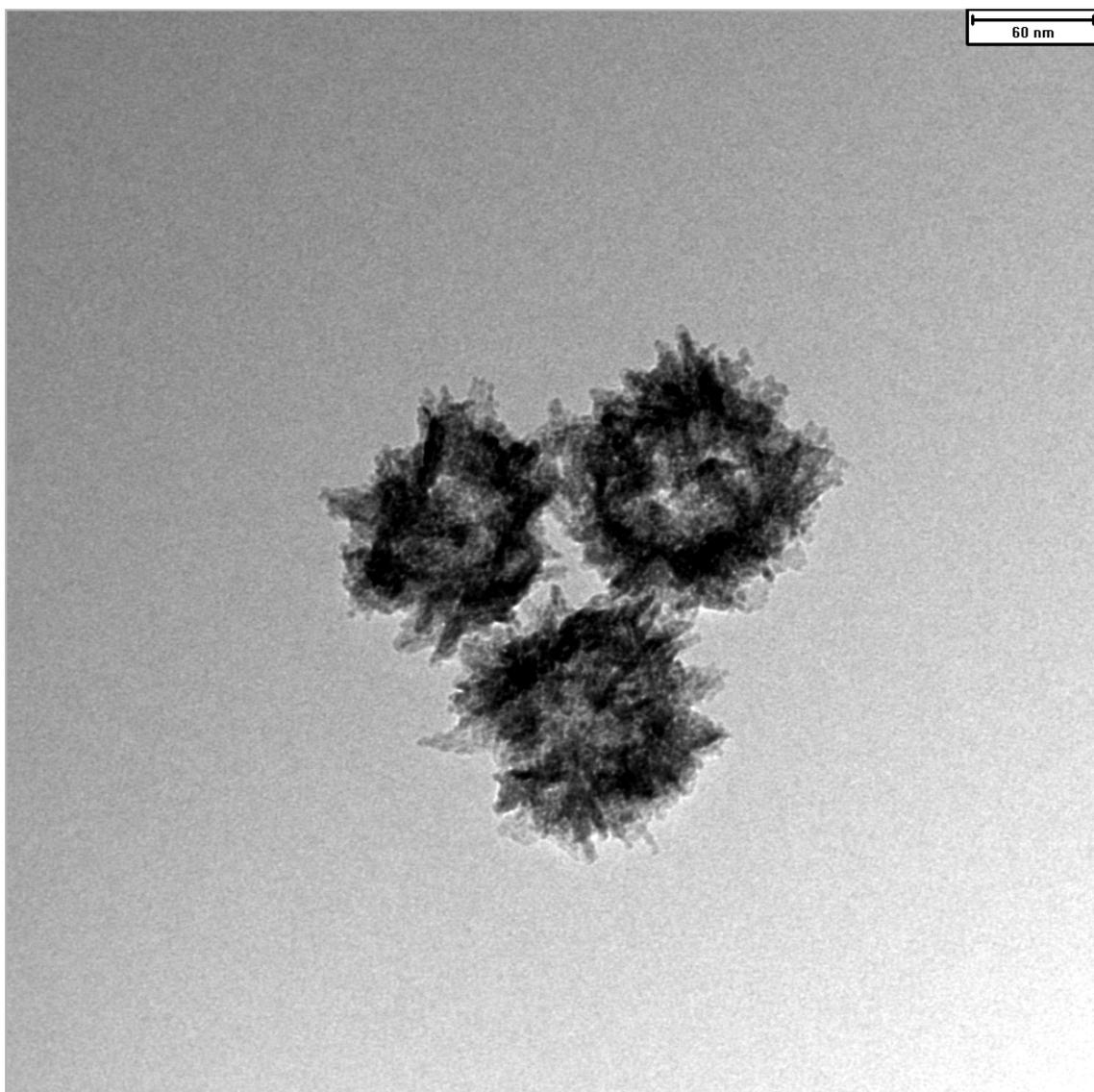


Figure S5. Magnified TEM images in Fig.2b.

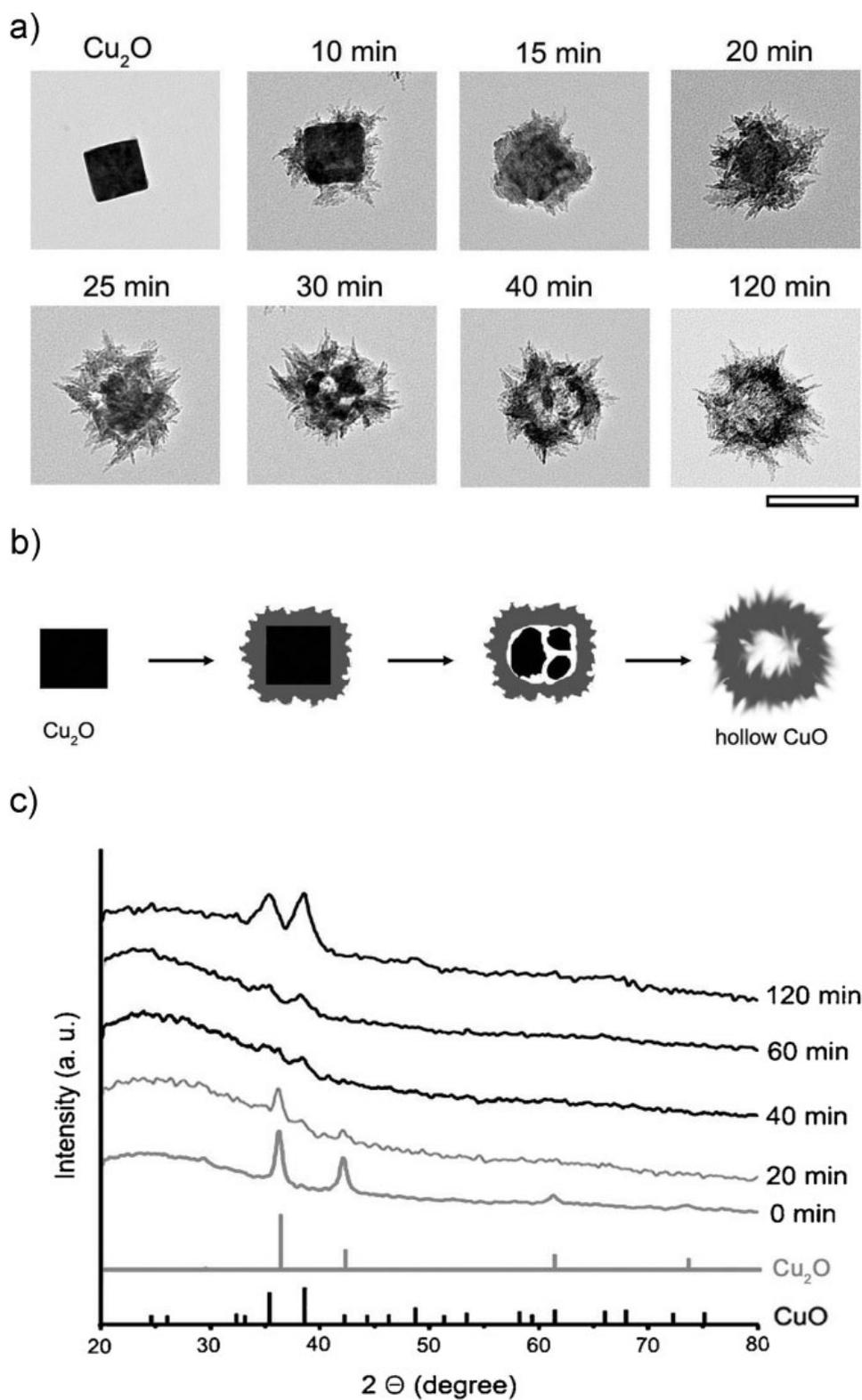


Figure S6. a) TEM images, b) shape-evolution scheme, and c) XRD spectral change over time during the oxidation of Cu_2O nanocubes.

IV. ¹H-NMR and ¹³C-NMR spectra of Products

