

Supporting information for

A Versatile Strategy to Selective Synthesis of Cu Nanocrystals and The *in situ* Conversion to CuRu Nanotubes

Xiaoqing Huang,[†] Yu Chen,[†] Chin-Yi Chiu,[†] Hua Zhang,[†] Yuxi Xu,[‡] Xiangfeng Duan,^{§§} and Yu Huang^{**§}
Email: yhuang@seas.ucla.edu

Experimental Details

Chemicals: Copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$, $\geq 99.99\%$), Ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot \text{H}_2\text{O}$, 99.98%), Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$), Iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\geq 99.0\%$), Ammonium chloride (NH_4Cl , 99.99%), Hexadecyltrimethylammonium chloride ($\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Cl})(\text{CH}_3)_3$, CTAC, $>98.0\%$), Poly(vinyl pyrrolidone) (PVP, $\text{MW} \approx 55000$), Benzyl alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, 99.8%), Formaldehyde (HCHO , 36.5-38% in H_2O), Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, AA, reagent grade), and Oleylamine ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_2\text{NH}_2$, 70%) were all purchased from Sigma-Aldrich. All the chemicals were used as received without further purification. The water (18 $\text{M}\Omega/\text{cm}$) used in all experiments was prepared by passing through an ultra pure purification system (Aqua Solutions).

Synthesis of Cu nanocubes: In a typical synthesis of Cu nanocubes, Copper (II) acetylacetonate ($\text{Cu}(\text{acac})_2$, 13.3 mg), Ammonium chloride (NH_4Cl , 0.27 mg), Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, 52.8 mg) and 5 mL Oleylamine were added into a vial. After the vial had been capped, the mixture was ultrasonicated for around 15 minutes. The resulting homogeneous mixture was then heated from room temperature to 170 °C in 15 min and kept at 170 °C for 3 hours in an oil bath before it was cooled to room temperature. The resulting colloidal products were collected by centrifugation and washed three times with a hexane/ethanol mixture.

Synthesis of Cu nanowires: In a typical synthesis of Cu nanowires, Copper (II) acetylacetonate ($\text{Cu}(\text{acac})_2$, 13.3 mg), Ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot \text{H}_2\text{O}$, 10.5 mg), Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, 52.8 mg) and 5 mL Oleylamine were added into a vial. After the vial had been capped, the mixture was ultrasonicated for around 15 minutes. The resulting homogeneous mixture was then heated from room temperature to 170 °C in 15 min and kept at 170 °C for 3 hours in an oil bath before it was cooled to room temperature. The resulting colloidal products were collected by centrifugation and washed three times with a hexane/ethanol mixture.

Synthesis of CuRu nanotubes: Typically, Copper (II) acetylacetonate ($\text{Cu}(\text{acac})_2$, 13.3 mg), Ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot \text{H}_2\text{O}$, 10.5 mg), Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, 52.8 mg) and 5 mL Oleylamine were added into a vial. After the vial had been capped, the mixture was ultrasonicated for around 15 minutes. The resulting homogeneous mixture was then heated from room temperature to 170 °C in 15 min and kept at 170 °C for 3 hours in an oil bath. After that, the mixture was further heated from 170 °C to 210 °C in 10 min and kept at 210 °C for 12 hours. The resulting colloidal products were collected by centrifugation and washed three times with a hexane/ethanol mixture.

Synthesis of hydrophilic Cu nanowires and nanocubes: In a typical synthesis of hydrophilic Cu nanowires, Copper (II) acetylacetonate ($\text{Cu}(\text{acac})_2$, 13.3 mg), Iron(III) chloride hexahydrate (FeCl_3 , 0.135 mg), poly(vinylpyrrolidone) (PVP, 80.0 mg) and 0.2 mL formaldehyde solution (36.5-38% in H_2O) were mixed together with 5 mL benzyl alcohol. After the vial had been capped, the mixture was ultrasonicated for around 15 minutes. The resulting homogeneous solution was transferred to a 20-mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 200 °C for 5 h before it was cooled to room temperature. The products were precipitated by acetone, separated via centrifugation and further purified by an ethanol-acetone mixture. The synthesis of Cu nanocubes was similar to that of nanowires except that FeCl_3 was replaced with NH_4Cl .

Characterization: TEM images were carried out on a FEI CM120 transmission electron microscope operated at 120 kV. High resolution TEM images and the high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM)-energy-dispersive X-ray spectroscopy (EDS) were taken on a FEI TITAN transmission electron microscope operated at 300 kV. The samples were prepared by dropping hexane dispersion of samples onto carbon-coated copper TEM grids (Ted Pella, Redding, CA) using pipettes and dried under ambient condition. Scanning electron microscopic (SEM) images were taken on a JEOL JSM-6700F with field emission gun. X-ray powder diffraction patterns were collected on a Panalytical X'Pert Pro X-ray Powder Diffractometer with $\text{Cu-K}\alpha$ radiation. The mole ratio of nanostructures was determined by the inductively coupled plasma atomic emission spectroscopy (TJA RADIAL IRIS 1000 ICP-AES).

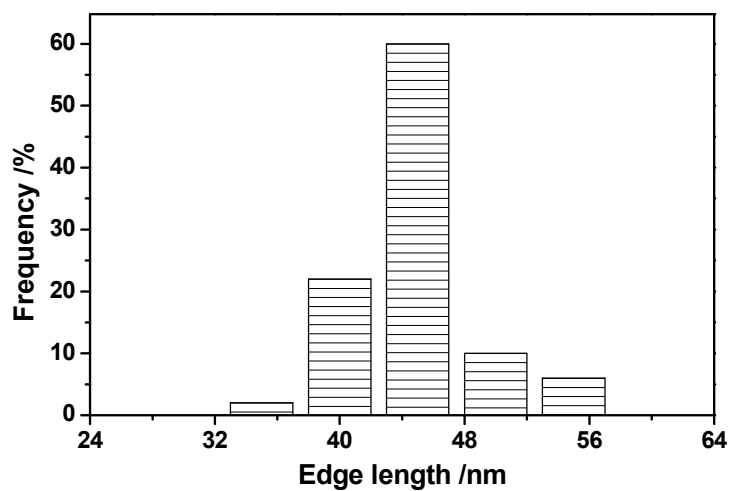


Figure S1. Edge length distribution of the Cu nanocubes shown in Figure 1.

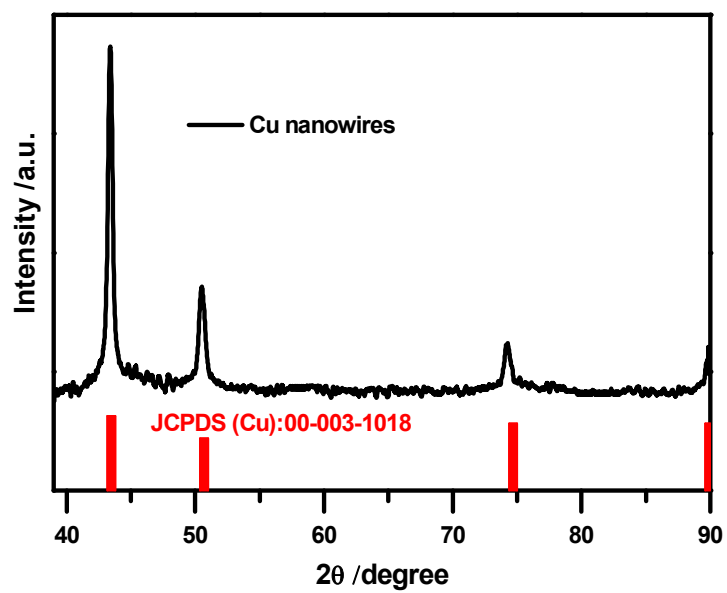


Figure S2. Representative XRD pattern of the ultralong Cu nanowires.

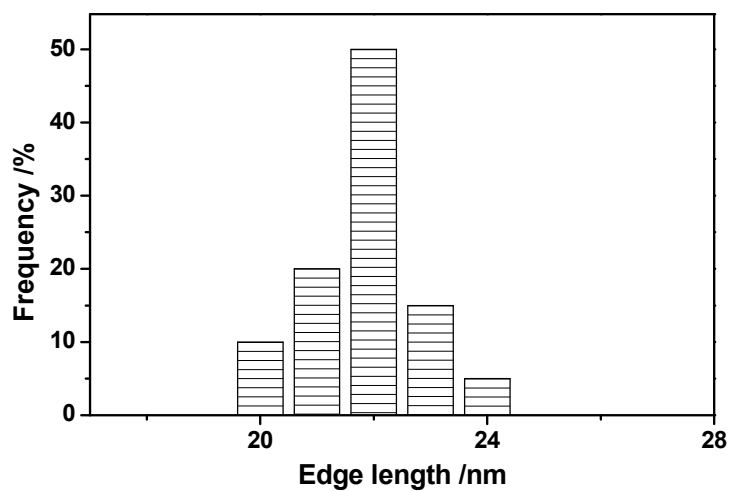


Figure S3. Diameter distribution of the Cu nanowires shown in Figure 2.

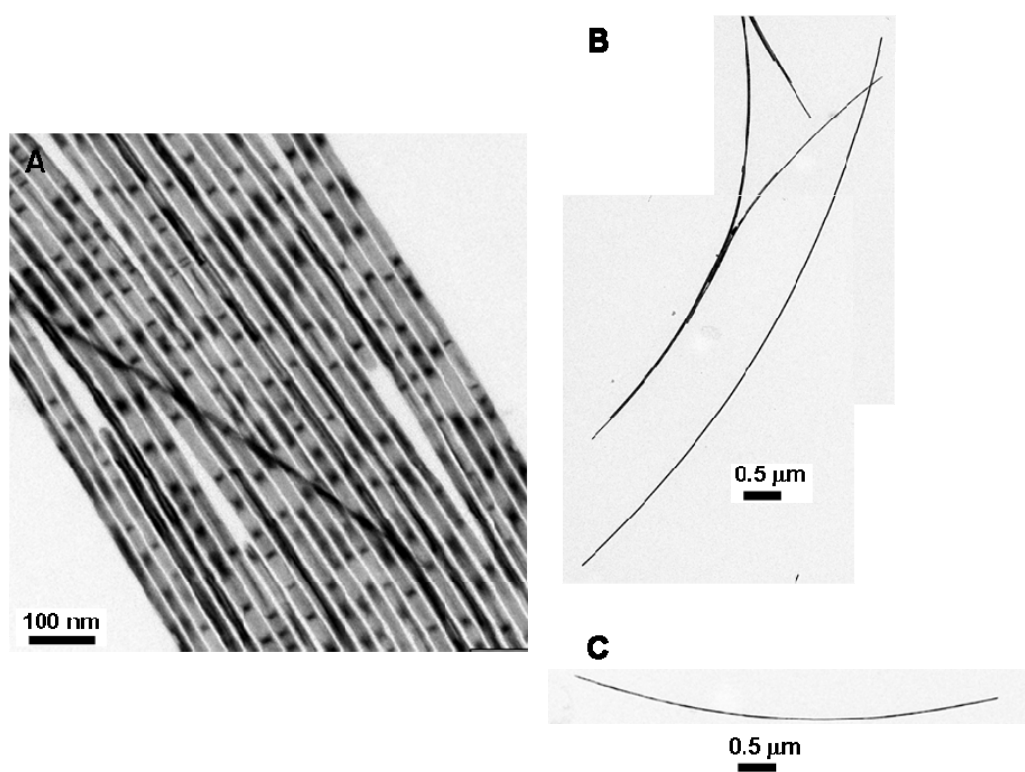


Figure S4. Additional images for ultralong Cu nanowires. (A) TEM of the Cu nanowires. (B, C) TEM images of several individual Cu nanowires.