A Rapid Synthesis of High Aspect Ratio Copper Nanowires for High-Performance Transparent Conducting Films

*Shengrong Ye, Aaron R. Rathmell, Ian E. Stewart, Yoon-Cheol Ha, Adria R. Wilson, Zuofeng Chen and Benjamin J. Wiley**

Department of Chemistry, Duke University, Durham, NC 27708, USA

E-mail: Benjamin.wiley@duke.edu

Synthesis of Copper Nanowires

In a typical copper nanowire synthesis, NaOH (15 M, 20 mL), $Cu(NO_3)_2$ (0.1 M, 1 mL) and EDA (1.5 - 4.5 mmol) were mixed at an elevated temperature (60 - 70 °C) for 3 minutes under stirring at 700 rpm. N_2H_4 (35 wt %, 0.12 - 0.22 mmol) was then added to the solution and the stirring was stopped after two minutes. The solution color changed from deep blue to clear and colorless to dark red, indicating the formation of thin Cu NWs. In the case of excessive N_2H_4 (e.g. N_2H_4 = 10.5 mM), the layer of the copper nanowires at the air-water interface turned pink 19 min after addition of N_2H_4. Otherwise, the Cu NWs floated to the air-water interface ~30 min after addition of N_2H_4 and remained dark red. The Cu NWs were extracted from the reaction solution by adding ~15 mL of an aqueous solution consisting of 3 wt % polyvinylpyrrolidone (PVP, MW 10,000) and 5 wt % diethylhydroxylamine (DEHA). After vigorously shaking and swirling this suspension, a layer containing the Cu NWs accumulated at the top of the suspension, and this layer was removed from the reaction solution with a separation funnel. The Cu NWs were further washed with a solution of 3 % PVP and 5% DEHA for three cycles of centrifugation (10 min at 2000 rpm) and decantation. To determine the yield of Cu NWs, the Cu NWs were dissolved in HNO_3, and the resulting solution was analyzed with an atomic absorption spectrometer (AAS, Perkin Elmer 3100).

In Situ Growth of Cu NWs

A mixture of NaOH (15 M, 20 mL), $Cu(NO_3)_2$ (0.1 M, 1 mL), EDA (2 and 4.5 mmol) and N_2H_4 (35 wt %, 0.42 mmol) was stirred at room temperature. The solution turned clear and colorless after 10 minutes and was used as the growth solution. Small aliquots (~6.5 μL) of the as-prepared growth solution were transferred to the cell made of two 22 mm × 22 mm coverslips (VWR, 0.17 mm thickness) spaced by a 120-μm-deep double sided adhesive well (Invitrogen, Secure-Seal^{TM} spacer, 9 mm diameter). The solution in the cell was then heated to the desired temperature (70 °C) on a transparent heater, and the growth of the nanowires was visualized and recorded through an optical microscope (Olympus BX51) fitted with a SC30 CMOS camera. Time lapsed images focused at the interface of the growth solution and the bottom coverslip were taken at a frame rate of 1 frame per second (fps) using the Olympus Stream imaging software. The lengths of each nanowire at different time points were measured with ImageJ.

Preparation of Transparent Conducting Films

Transparent conducting films of Cu NWs were made in a manner similar to previous work.[1] The Cu NWs were transferred from the storage solution (3% PVP and 5% DEHA) into a 1.5 mL centrifuge tube after the initial washing steps. This suspension was centrifuged at 2000 rpm for 1 min. The Cu NWs were washed 3 times using a solution of 3% DEHA to ensure PVP was removed. After the PVP was removed, the Cu NWs were washed with ethanol to remove the majority of the water and then washed once more with the nitrocellulose based ink formulation. The Cu NWs were re-dispersed in the ink by vortexing to form a homogeneous suspension. To prepare a transparent nanowire electrode, glass microscope slides were placed onto a clipboard to hold them down while the nanowire ink (50 μL) was pipetted in a line at the top of the slide. A Meyer rod (Gardco, 51.3 μm wet film thickness) was then quickly (< 1 second) pulled down over the nanowire ink by hand, spreading it across the glass into a thin, uniform film. Different densities of nanowires on the surface of the substrate were obtained by varying the concentration of the nanowires in the ink. The film was dry after approximately 60 seconds. To remove organic material from the nanowire network, the films were cleaned in a plasma cleaner (Harrick Plasma PDC-001) for 10 minutes in an atmosphere of 95% N_2 and 5% H_2 at a pressure of 600-700 mTorr. The nanowire films were then heated at 225 °C in a tube furnace for 30 minutes under a

---

[1] A. R. Rathmell, B. J. Wiley, *Adv. Mater.* **2011,** *23*, 4798.

constant flow of H_2 (350 mL min^{-1}) to anneal the wires together and decrease the sheet resistance. The transmittance and sheet resistance of each nanowire film was measured using a UV-Vis-NIR spectrophotometer (Cary 6000i) and a four-point probe (Signatone SP4-50045TBS). Each data point in Figure 5 is the average of 5 measurements.

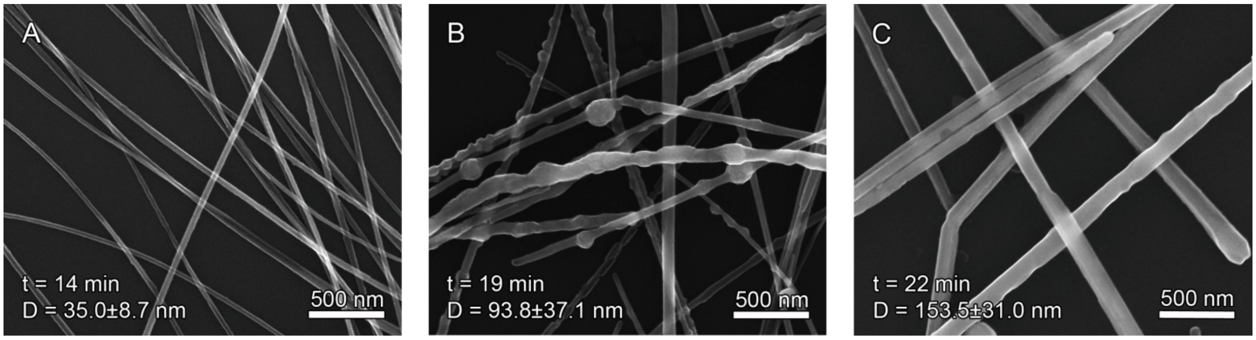

Fig. S1 SEM images of Cu NWs grown with 10.5 mM of N_2H_4, and collected at reaction times of (A) 14 min, (B) 19 min, and (C) 22 min, respectively.

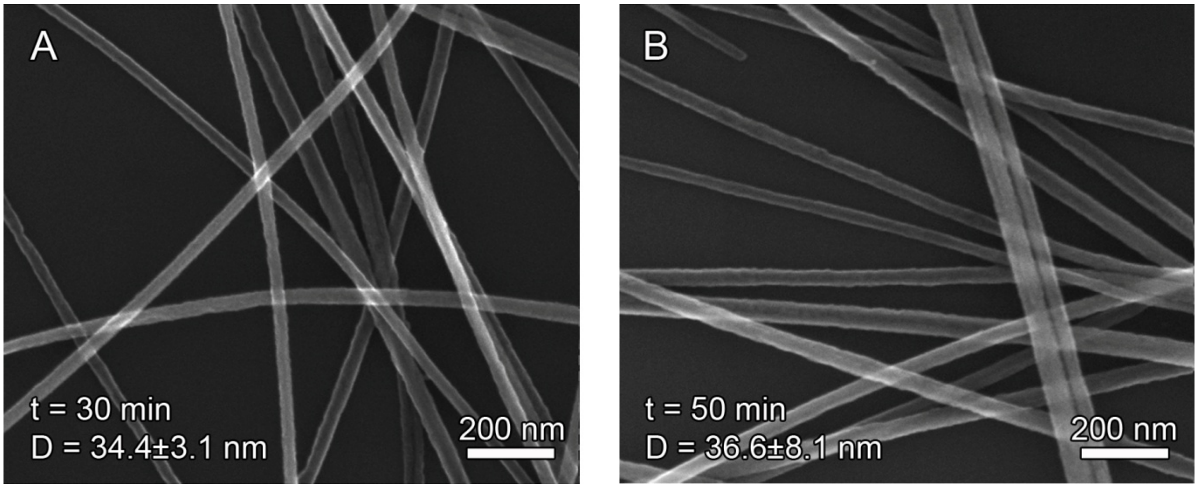

Fig. S2 SEM images of Cu NWs collected at reaction times of (A) 30 min, and (B) 50 min show that running the reaction with a reduced amount of N_2H_4 (5.7 mM) prevents the increase in diameter observed at higher hydrazine concentrations.

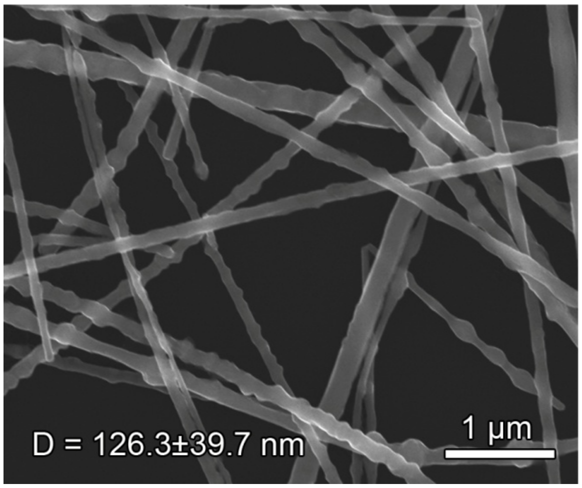

Fig. S3 Cu NWs with particle-like structures along their length formed at a N_2H_4 concentration of 6.2 mM after a reaction time of 30 min.

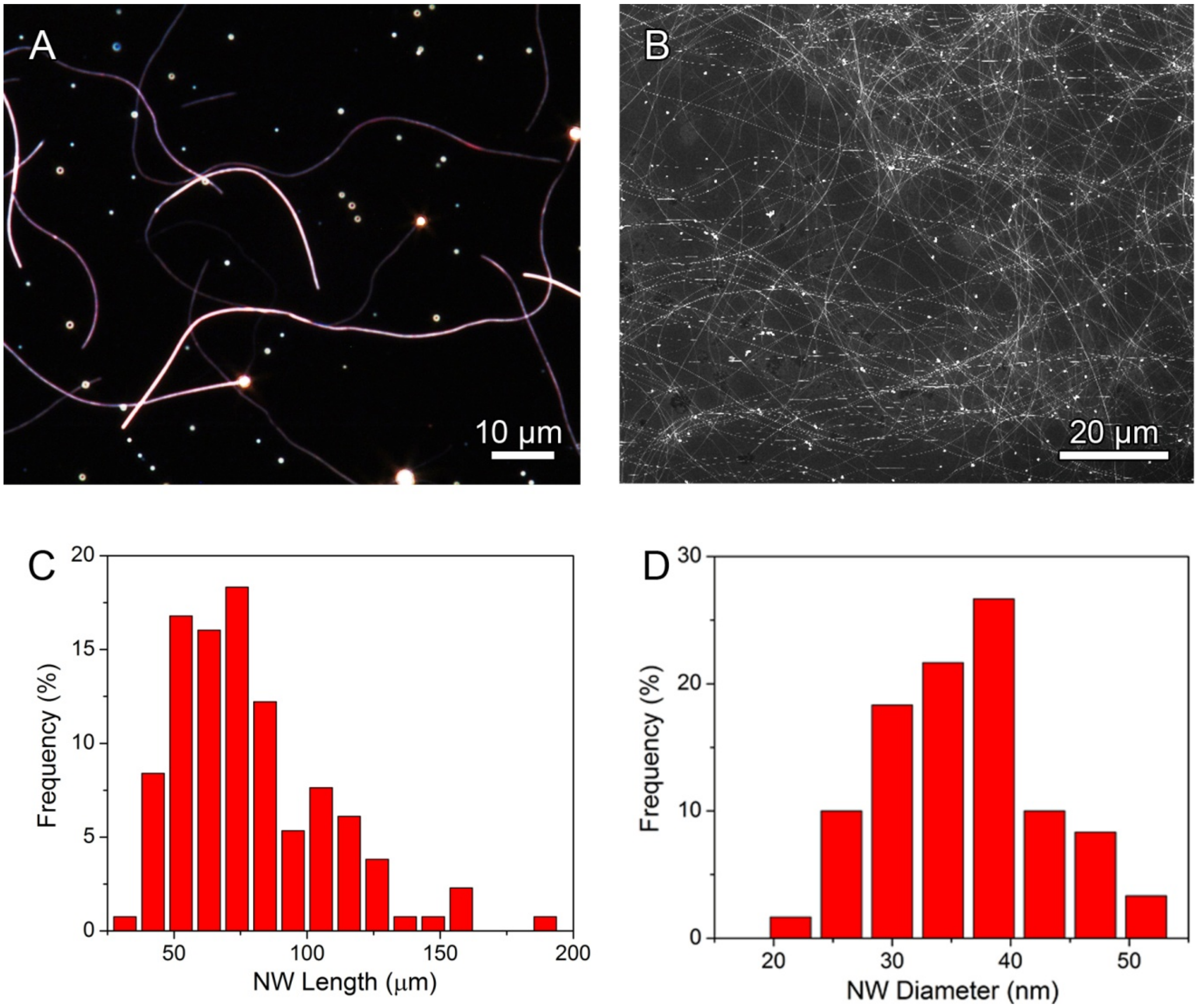

Fig. S4 Dark field optical microscope (A) and SEM (B) images of Cu NWs synthesized at 60 °C with a length of 79.8 ± 30.6 µm (C) and a diameter of 36.1 ± 6.6 nm (D).

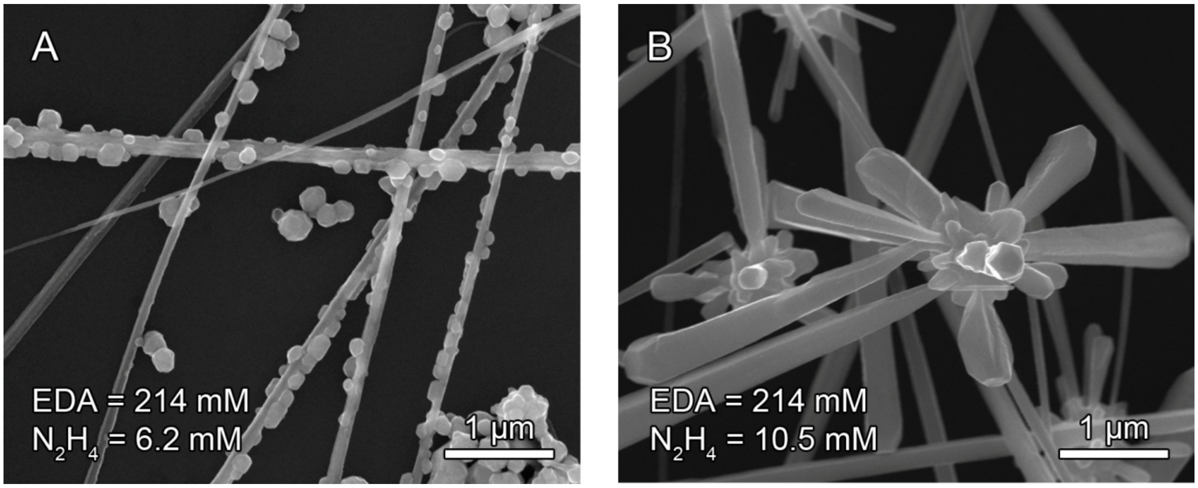

Fig. S5 Tapered Cu NWs also undergo (A) partial and (B) complete thickening at an N_2H_4 concentration of 6.2 and 10.5 mM, respectively.