

Supporting Information

Ultralow-Density Copper Nanowire Aerogel Monolith with Tunable Mechanical and Electrical Properties

*Yue Tang^{1,2}, Kai Leng Yeo^{1,2}, Yi Chen^{1,2}, Lim Wei Yap^{1,2}, Wei Xiong^{1,2} and Wenlong Cheng^{*1,2}*

¹ Department of Chemical Engineering, Monash University, Clayton, Victoria 3800 (Australia)

² The Melbourne Centre for Nanofabrication, Clayton, Victoria 3168 (Australia)

1. Experimental Details

Materials: Copper (II) nitrate pentahemihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, $\geq 98\%$), ethylenediamine (EDA, BioXtra), hydrazine solution (N_2H_4 , 35 wt.% in H_2O), polyvinylpyrrolidone (PVP, MW = 10,000), (Heptadecafluoro-1,1,2,2-tetradecyl)trimethoxysilane (FAS, $\geq 98\%$), and Oil Blue N (dye content 96%) were purchased from Sigma-Aldrich. Sodium hydroxide ($\geq 99.5\%$), ethanol (96%), chloroform (99.0% - 99.1%), toluene ($\geq 99.9\%$), and hexane ($\geq 98\%$) were obtained from Merck. Unleaded #91 gasoline was obtained from Shell fuel station in Australia. PELCO[®] colloidal silver was purchased from Ted Pella, Inc. All of these chemicals were used as received.

Characterization: Freeze drying process was performed on an HETO PowerDry PL6000 Freeze Dryer. The dimensions of CuNW aerogel monoliths were measured by a Stamvick caliper with an accuracy of 0.01 mm, and the weight of the samples were checked through a METTLER TOLEDO balance (MS 105DU) with an accuracy of 0.01 mg. Network structures of CuNW monoliths were observed on an FEI Nova NanoSEM 430 field emission gun scanning electron microscope (SEM) operated at an acceleration voltage of 2 kV and a working distance of 4-5 mm. Conductivity of CuNW monoliths was checked through a two-probe technique. A thin layer of liquid silver colloid was employed to optimize the electrical contact between CuNW monoliths and aluminum foils, and the resistance was measured by a multi-meter. Mechanical properties of cylindrical shaped CuNW aerogel monoliths were measured by a Micro Tester Instron (5848) using a 10 N load cell and strain control mode with a strain rate of $100\% \text{ min}^{-1}$. Contact angle tests were used to evaluate the wetting properties of CuNW monoliths before and after FAS modification. Droplets with the volume of 2 μL were employed to measure the contact angles through contact angle analysis system from JANDEL (MODEL RM3) at room temperature. Every contact angle result was a mean value from five times of measurements on different places.

Preparation of CuNWs: NaOH (20 mL, 15 M), $\text{Cu}(\text{NO}_3)_2$ (1 mL, 0.1 M), EDA (0.15 mL), and N_2H_4 (0.025 mL, 35 wt%) were mixed in sequence in a 50 mL round bottom

flask. Then, the solution was heated to 80 °C under a stirring speed at 200 rpm. After the mixture turned into colorless, the solution was transferred into a 50 ml centrifuge tube immersed in an ice bath, and 5 ml PVP (0.4 wt%) aqueous solution was added to the top of the reaction solution gently. CuNWs floated on the top of the reaction solution after 1 hour of growth. Then, they were re-dispersed in an aqueous washing solution (WS1) containing N₂H₄ (3 wt%) and PVP (1 wt%). The combined solution was centrifuged at 2,000 rpm for 5 minutes, and the precipitated CuNWs were then re-dispersed in new WS1 by vortexing at 3,000 rpm for 30 seconds. The purification process was repeated by three times to eliminate redundant reaction agents. To remove the excess PVP, CuNWs were re-dispersed in WS2 containing only N₂H₄ (3 wt%) and centrifuged at 2,000 rpm for 5 minutes twice. Finally, after three times of purification by deionized water via centrifugation at 2,000 rpm for 5 minutes, CuNW aqueous solution was ready to freeze.

Fabrication of CuNW aerogel monolith: CuNW aqueous solution was pour into a glass vial (50 × 12 mm) and left in a freezer with the temperature of -80 °C for at least 2 hrs. Then the frozen sample was freeze-dried at a sublimation temperature of -47.4 °C and a pressure of 0.10 KPa.

FAS modification process: The superhydrophobic CuNW aerogel monoliths were generated by silanizing CuNW monoliths with FAS in a vacuum desiccator under decompression environment at 80 °C for 3 hrs.

2. Fabrication of CuNW aerogel monoliths

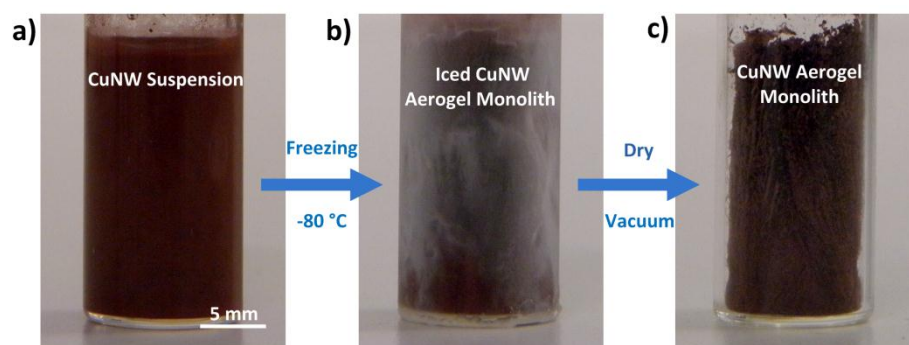


Figure S1 Photographic images showing the fabrication of CuNW aerogel monoliths.

No obvious shrinkage was observed before and after freeze drying process.

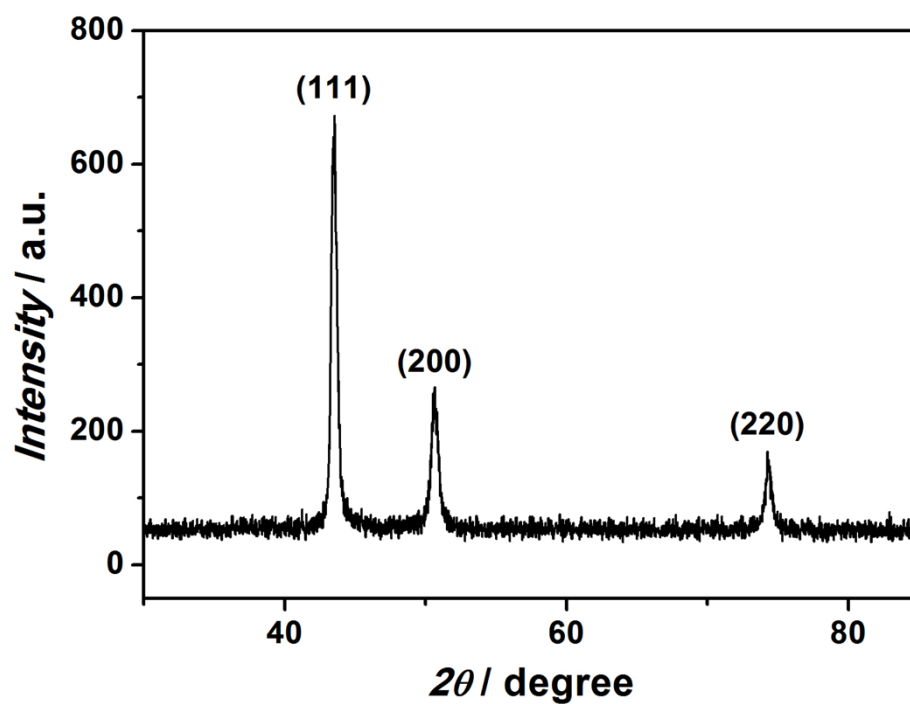


Figure S2 XRD patterns of CuNW aerogel monoliths. The patterns are identical to those from separated CuNWs without freeze drying, which indicated that the fabrication process did not vary the crystalline structures of CuNWs.

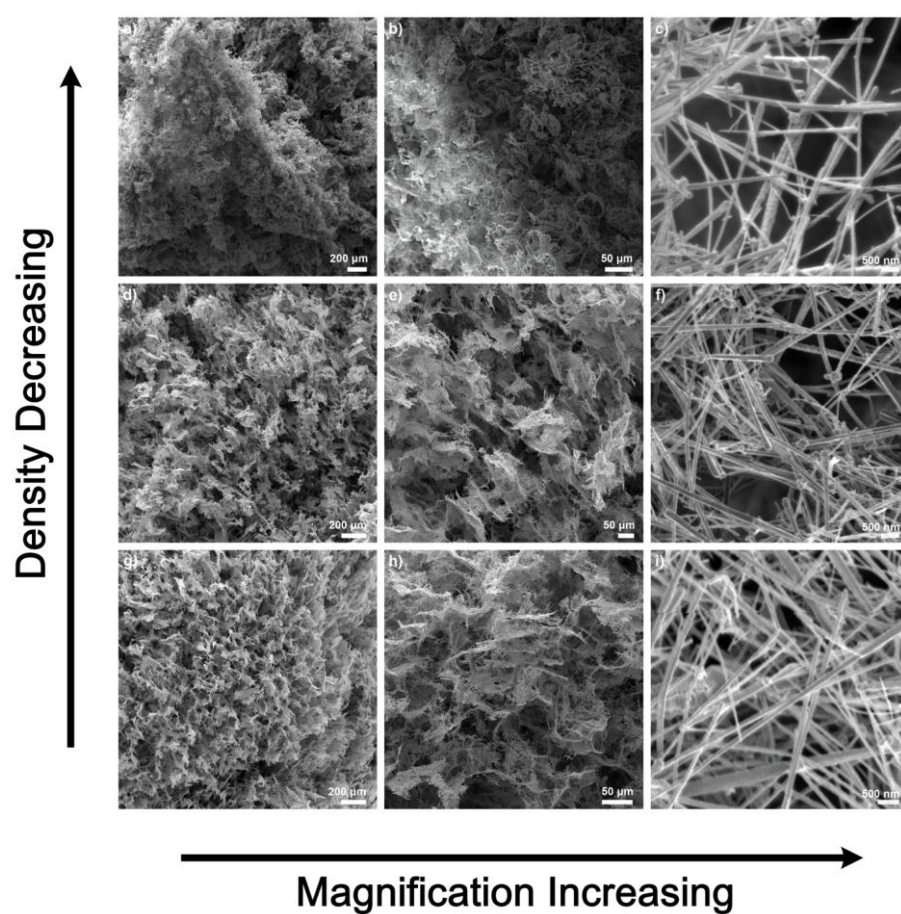


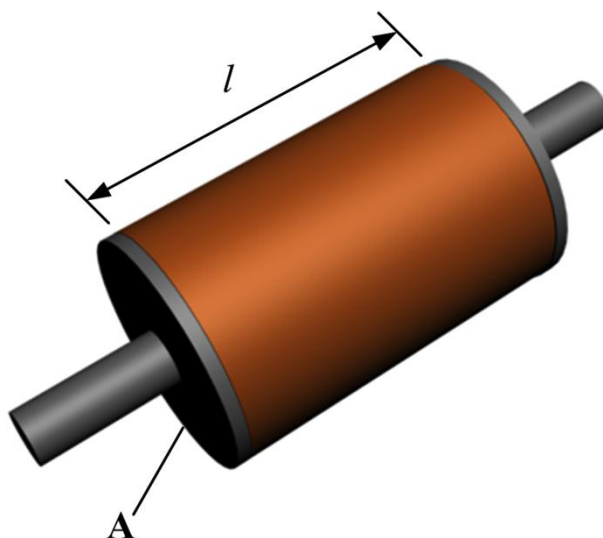
Figure S3 SEM images of CuNW aerogel monoliths with different densities: (a-c) 4.6 mg cm^{-3} , (d-f) 8.3 mg cm^{-3} , (g-i) 13.5 mg cm^{-3} under various magnifications.

3. Electrical conductivity of CuNW aerogel monoliths

The electrical conductivity of CuNW aerogel monoliths (σ) was calculated from eq. (S1).

$$\sigma = \frac{l}{RA}$$

where l was the length, R referred to the electrical resistance, and A was the cross-sectional area of CuNW aerogel monoliths (Scheme S1).



Scheme S1 A scheme depicted how we measured and calculated the conductivity of CuNW aerogel monoliths.

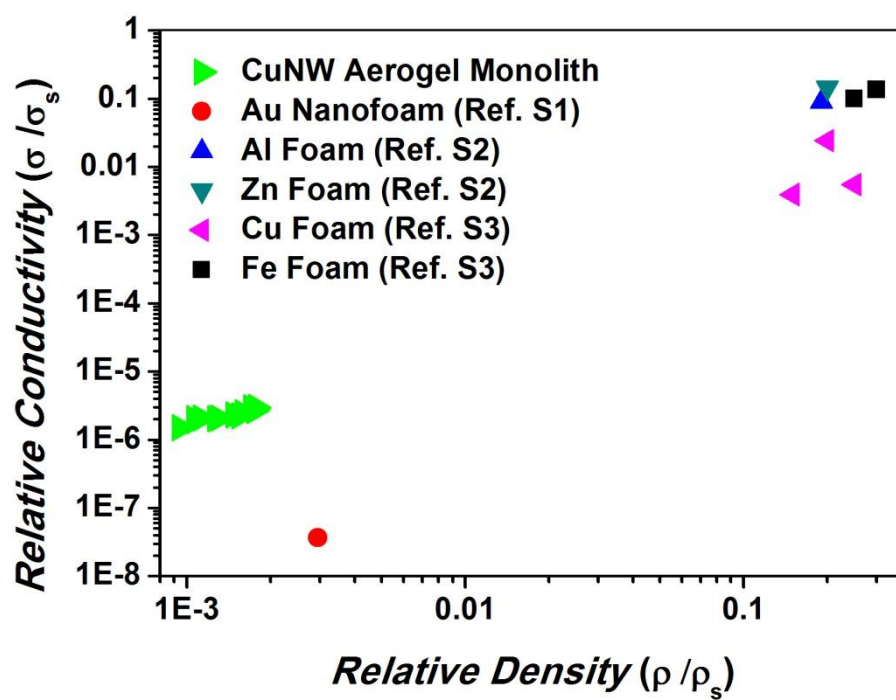


Figure S4 Relative electrical conductivity of CuNW aerogel monoliths in comparison with other porous metallic materials, such as Au nanofoams,¹ Al foams,² Zn foams,² Cu foam,³ and Fe foams.³

4. Young's Modulus of CuNW aerogel monoliths

We used Young's modulus to evaluate the mechanical properties of CuNW monoliths, which indicated the stiffness of the materials in elastic regions. The slopes of the stress-strain curves in linear regions (from 0% to 10% strain) of CuNW monoliths were employed to derive the Young's modulus. The dimensions of CuNW aerogel monoliths were measured through a Stamvick caliper with an accuracy of 0.01 mm and the weights of them were obtained from a METTLER TOLEDO balance (MS 105DU) with an accuracy of 0.01 mg. The volumes (V) of cylindrical shaped CuNW aerogel monoliths were calculated based on eq. (S2):

$$V = \pi \left(\frac{d}{2}\right)^2 h$$

d refers to the diameter of CuNW monoliths, and h represents the height of CuNW aerogel monoliths. The densities (D) of CuNW monoliths were calculated from eq. (S3):

$$D = \frac{m}{V}$$

m and V are the mass and volume of CuNW aerogel monoliths, respectively.

5. References

1. B. C. Tappan, S. A. Steiner and E. P. Luther, *Angew. Chem. Int. Ed.*, 2010, **49**, 4544.
2. Š. B. J. Kováčik and J. Bielek, in *Cellular Metals and Metal Foaming Technology*, MIT-Verlag 2001.
3. X. Ma, A. J. Peyton and Y. Y. Zhao, *NDT & E International*, 2006, **39**, 562.