Supplementary Information

Size-dependent thermal oxidation of copper: single-step synthesis of hierarchical nanostructures

Christopher J. Love, J. David Smith, Yuehua Cui, Kripa K. Varanasi*

**Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

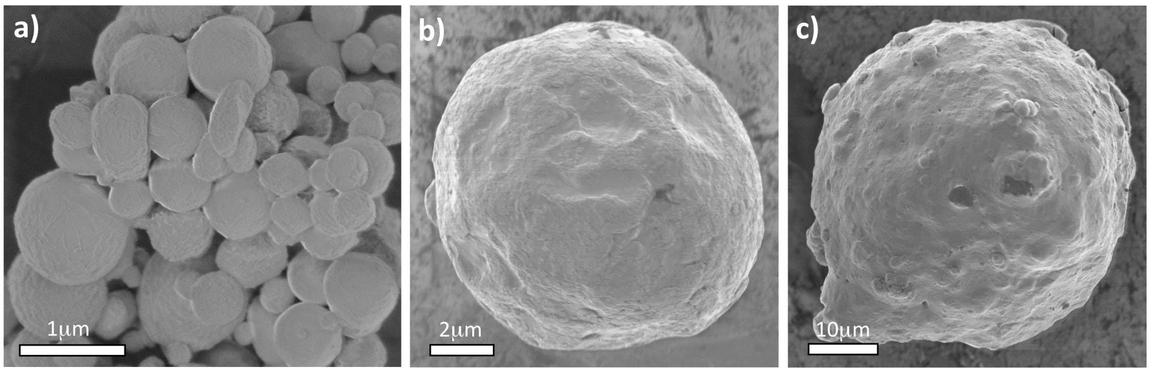

Figure S1. Unprocessed copper powder. a) 1μm, b) 10μm, and c) 50μm. Prior to thermal oxidation, all particles are smooth and absent of nanowires.

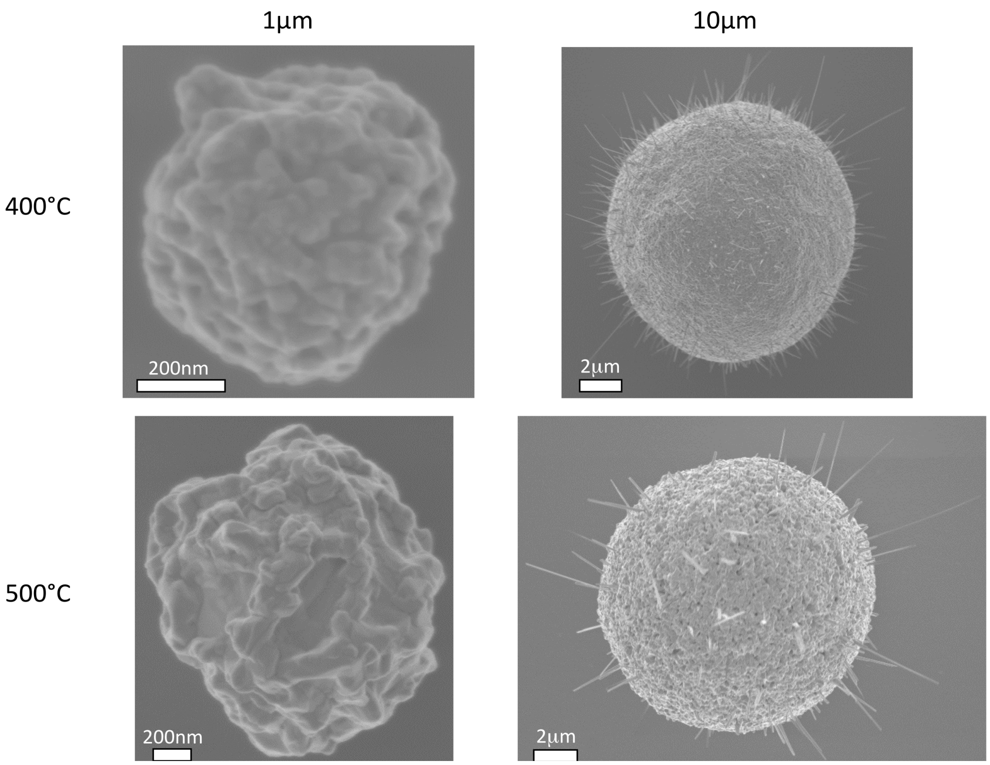

Figure S2. SEM images of 1μm and 10μm particle sizes at 400˚C and 500˚C. Similar to our results at 600°C (Figure 1), we observe little to no nanowires on the 1μm particles, but the larger 10μm particles are covered by nanowires.

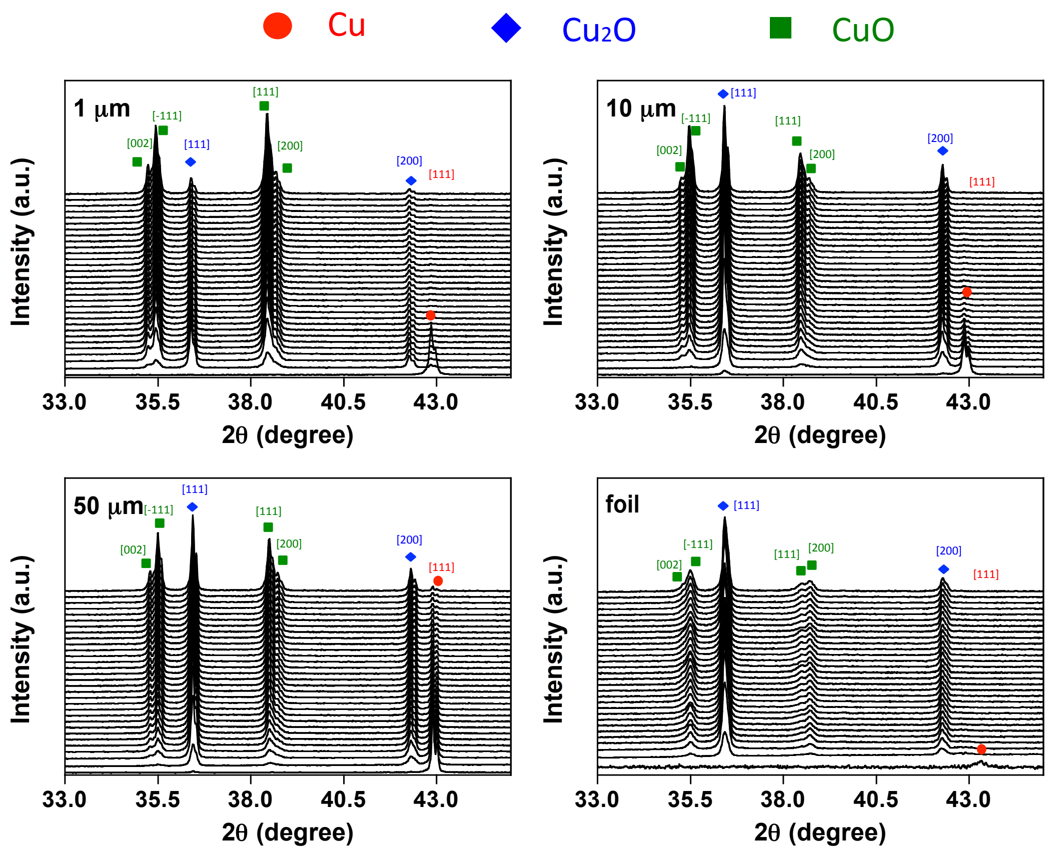

Figure S3. Raw in-situ XRD time scans of copper samples revealing variations in oxidation product formation based on size.

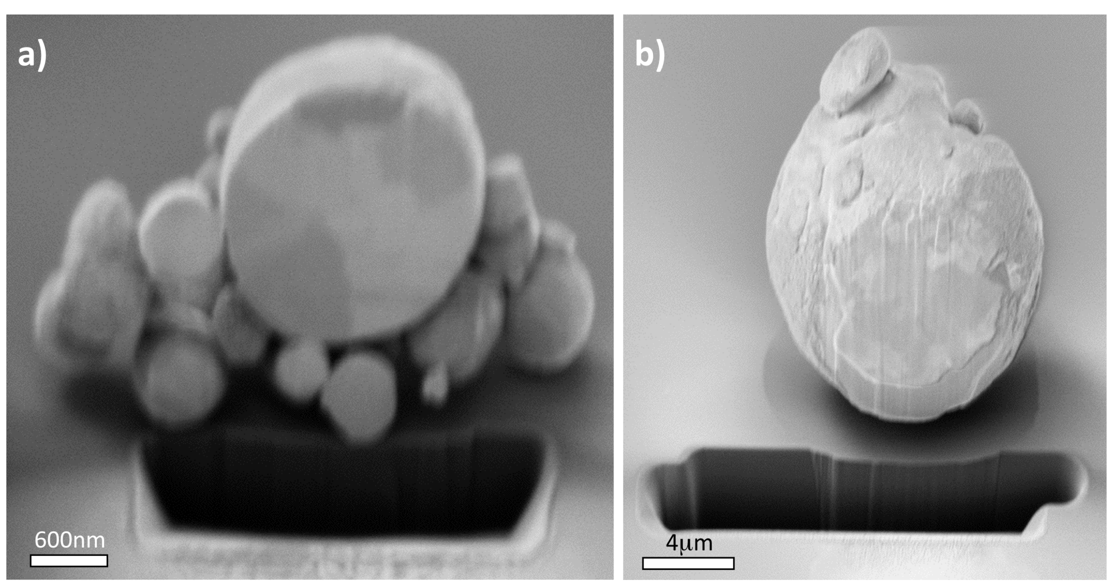

Figure S4. FIB control revealing solid cross-sections of an unoxidized a) 1μm and b) 10 μm copper particle.

Calculation of minimum initial copper particle size needed to reach a critical CuO layer thickness required for nanowire growth

An upper limit for the CuO oxide shell thickness that can be formed from a copper particle is calculated by considering the limiting case of complete oxidation of Cu to CuO. The relative change in volume resulting from the oxidation is determined from the known molecular mass, M, and density, ρ, of the Cu and CuO:

$$\frac{V_{CuO}}{V_{Cu}} = \frac{M_{CuO}/\rho_{CuO}}{M_{Cu}/\rho_{Cu}} = 2.28 \qquad (1)$$

Here we assume an approximately spherical copper particle of initial radius r_i. According to Yuan's model*, copper ions diffuse through the Cu_2O and CuO shells to react at the Cu_2O/CuO interface and the CuO interface with the environment. Since no reaction occurs at the Cu/Cu_2O interface, the position of the Cu/Cu_2O interface is expected to remain approximately constant at r_i. The volume ratio of a copper shell with thickness t and inner radius r_i to the initial copper particle of radius r_i is given by:

$$\frac{V_{CuO}}{V_{Cu}} = \frac{\frac{4}{3}\pi[(r_i + t)^3 - r_i^3]}{\frac{4}{3}\pi r_i^3} = \left(1 + t / r_i\right)^3 - 1 \qquad (2)$$

By equating the right-hand side of Eq. 1 and 2, we can solve for a lower limit on the radius of the initial copper particle required to obtain a CuO shell of thickness t. The resulting radius is $r_i = 2.04t$, or in terms of the initial particle diameter, d_i,

$$d_i \approx 4t \qquad (3)$$

According to Yuan et al., CuO nanowire growth does not begin until the CuO layer reaches a critical thickness of around $t_{cr} \approx 1$ μm*. Therefore from Eq. 3, we predict a cut-off diameter below which there is no appreciable nanowire growth of approximately 4 μm. Other papers have reported nanowire growth on flat substrates as thin as 0.5 μm**, and thus the cut-off particle diameter may be as low as around 2 μm.

* Lu Yuan, Y. W., Rediola Mema, Guangwen Zhou. *Acta Materialia* **2011,** 59, 2491-2500.

** Park, Y.-W.; Seong, N.-J.; Jung, H.-J.; Chanda, A.; Yoon, S.-G. *Journal of The Electrochemical Society* **2010,** 157, (6), K119.