

Copper Nanoparticle Synthesis and Characterization

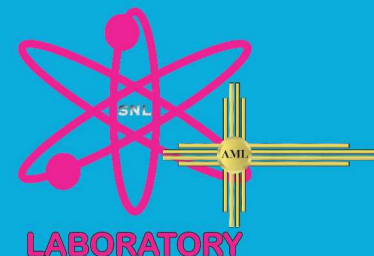
Jeremiah M. Sears,
Timothy J. Boyle,
Nelson S. Bell,
Adam W. Cook,
LaRico J. Treadwell,
Francesca Fasulo,
Benjamin Hammel,
Jessie Linder,
Thao Ngyuen

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in the national interest*



ADVANCED MATERIALS



LABORATORY

Sandia National Laboratories
Advanced Materials Laboratory

1001 University BLVD, SE
Albuquerque, NM 87106

jmsears@sandia.gov

(505)272-7049



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Direct write explained

A suite of layerwise additive manufacturing techniques for deposition of enabling materials



OPTOMECH
Production Grade 3D Printers... with a Material Difference



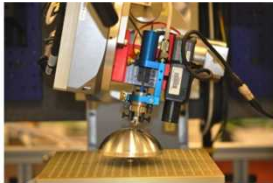
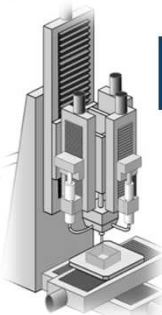
sonoplot



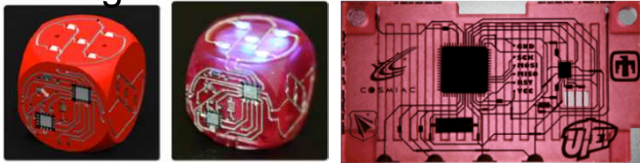
SCRIPT



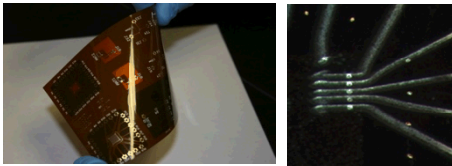
- Extremely broad materials compatibility (1-1,500,000 cP)
- Supports 3D printing and conformal depositing to 1 micron
- Readily supports component fabrication via deposition of enabling materials and integration of ASICs



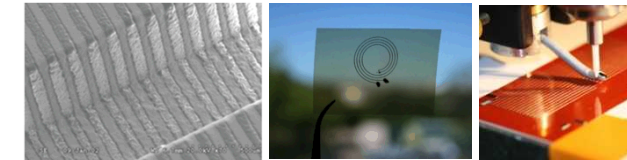
Nordson
EFD



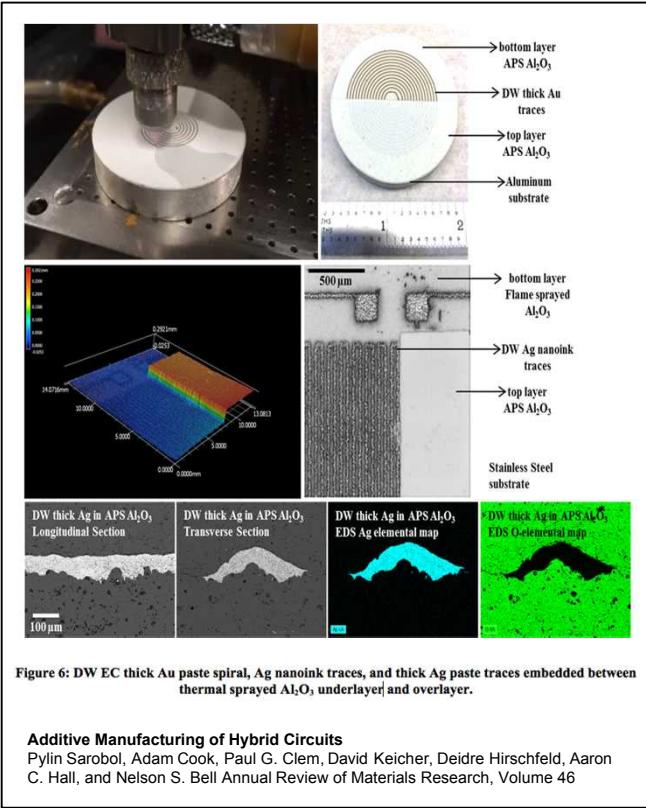
ASIC integration using DW metallization, W.M. Keck Center for 3D Innovation



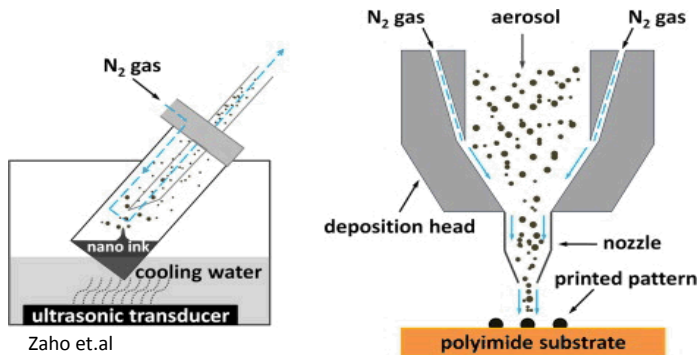
Printed wire bond replacement at die level interface



Nanoparticle ink printing on non-planar and thermally sensitive substrates

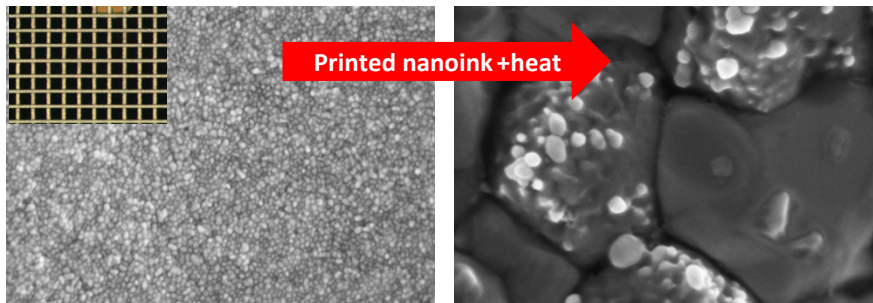
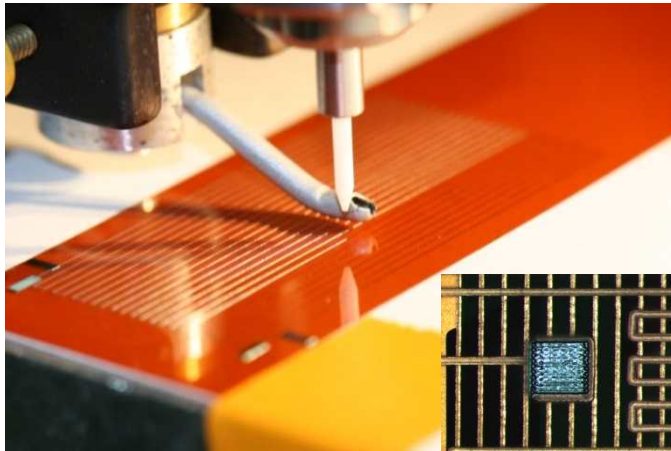
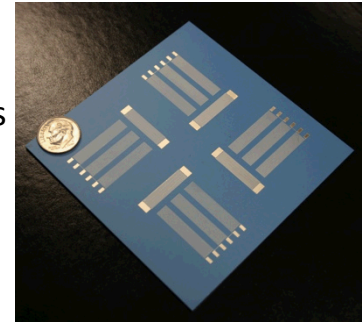


Direct Write Printing by Aerosol Jet



Aerosol Jet Printing Method (Optomec)

- Aerosol can be focused using inert gas streams and a small nozzle
- Atomization of liquid ink to produce a dense aerosol mist
- Line widths as narrow as $10\text{ }\mu\text{m}$ with $0.5\text{--}3\text{ }\mu\text{m}$ heights (silver nanoink)
- Broad materials compatibility
- Expanded post processing capabilities
- Rapid design iteration



- DC and RF pathways for interconnect and antenna applications on planar or arbitrary surfaces
- Strain and crack sensors for structural health monitoring, resistance temperature devices (RTD)
- Integration of packaged components with external sensing networks for value added functionality

Ink Problems

Commercial Inks

- Storage issues
- Not uniform (often have clumps)



Our Synthetic method allows

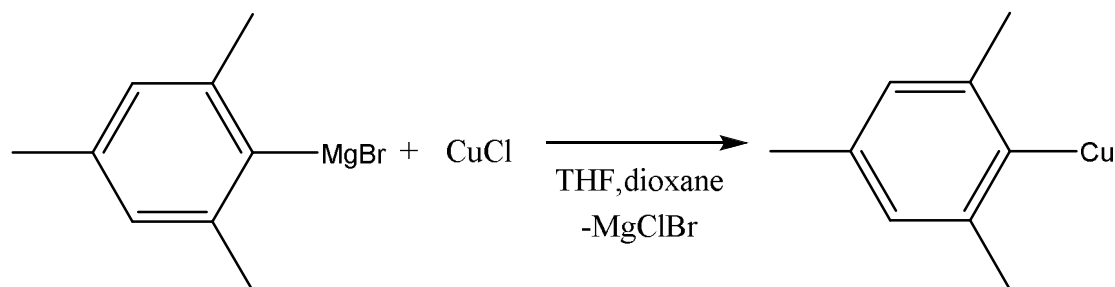
- Stable, uniform particles
- Tunable product

Cu Interest

- Price
- Similar properties to the other coinage metals
- Customer Interest



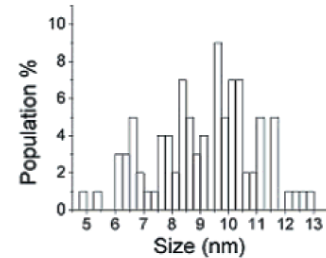
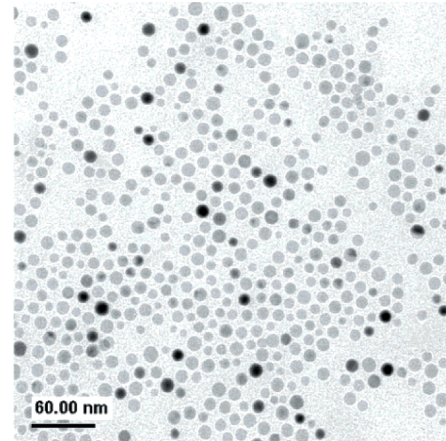
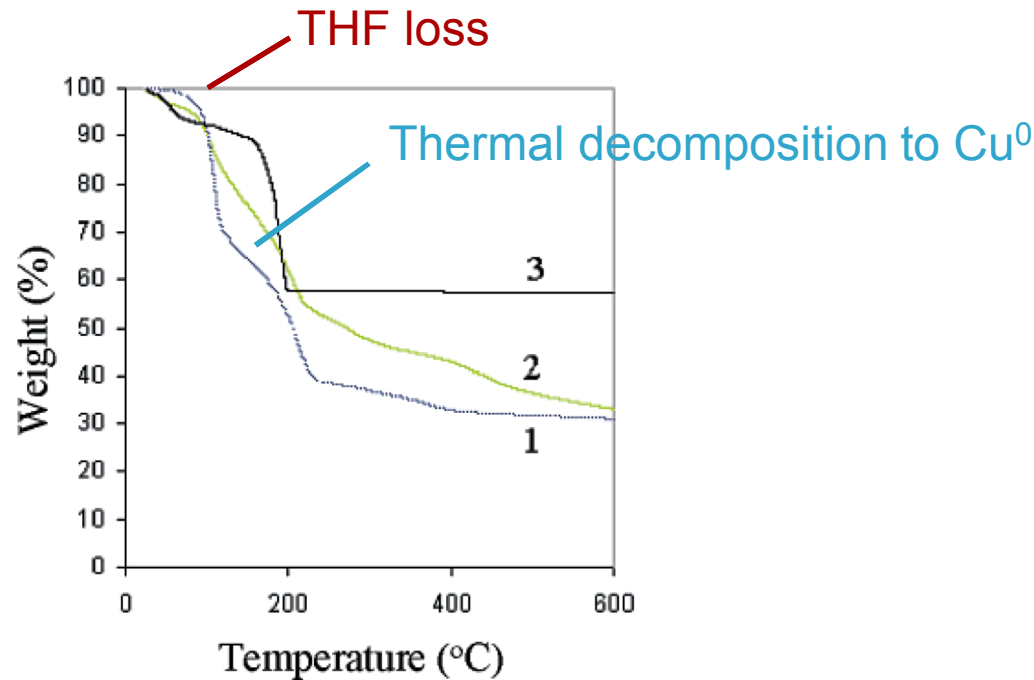
Metal Chloride Metathesis



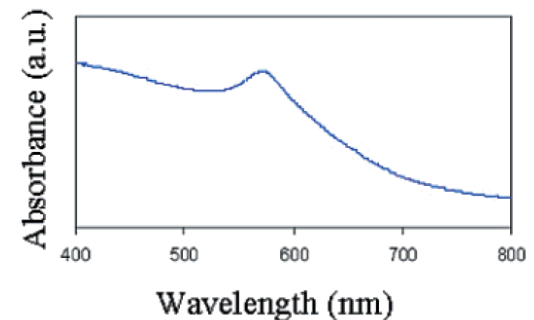
^1H NMR Spectroscopy
 δ 1.47, 1.34, 1.24 ppm

- High product yield
- Scalable up to 50 g

The Old Way to Make Cu NP

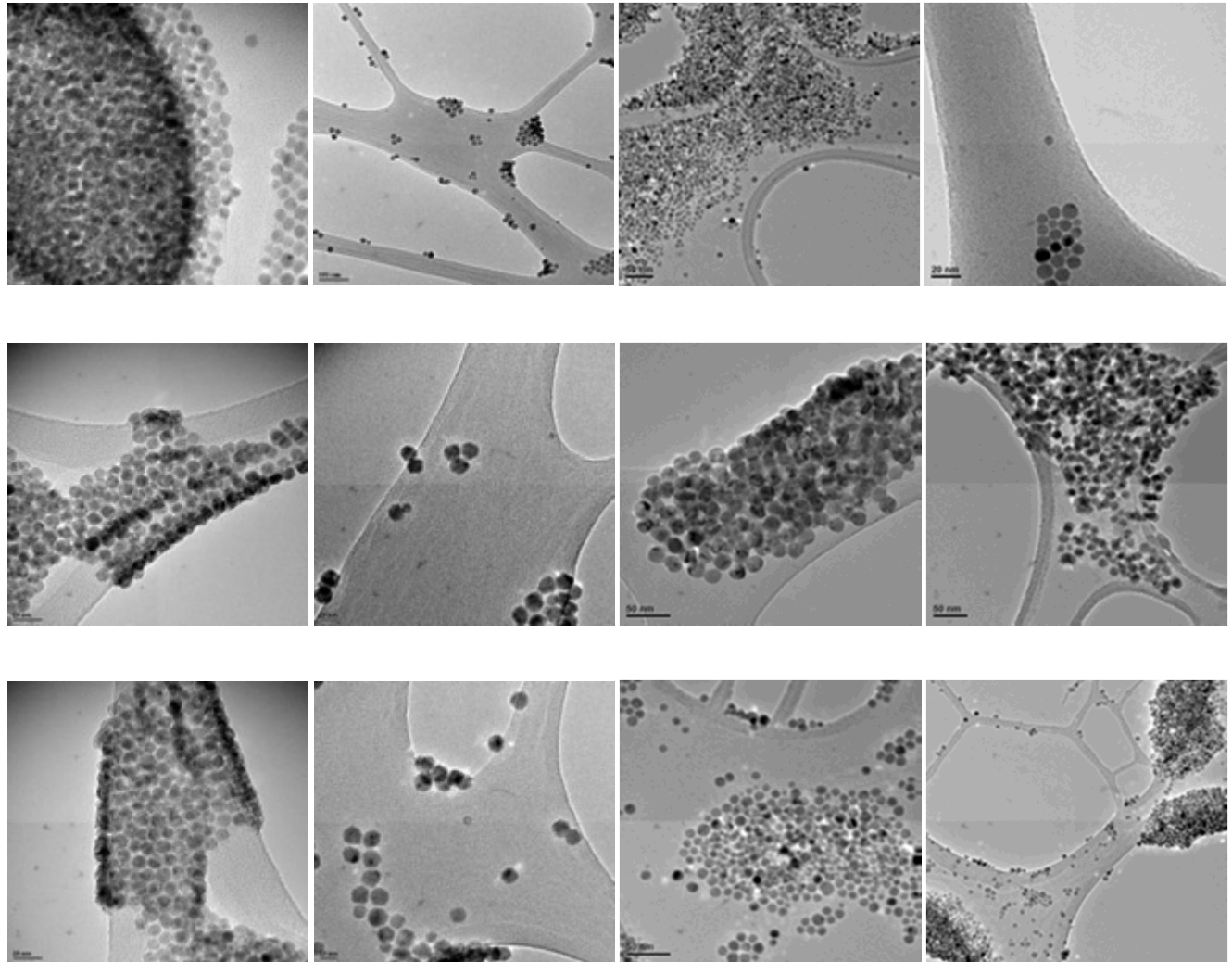


- TGA analysis (Cu (1), Ag (2), and Au (3)) for suitable solvent injection temperature
- Addition of Cu(Mes) in 8N to a 300 °C HDA solution
- Held at 225 °C for 30 min, cool to rt
- Wash MeOH, extract with Tol

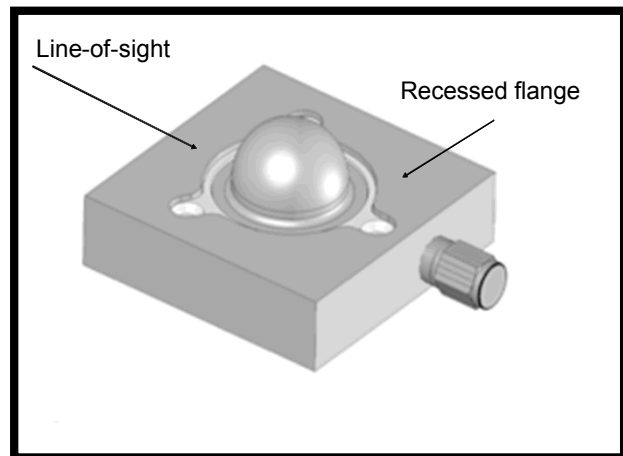
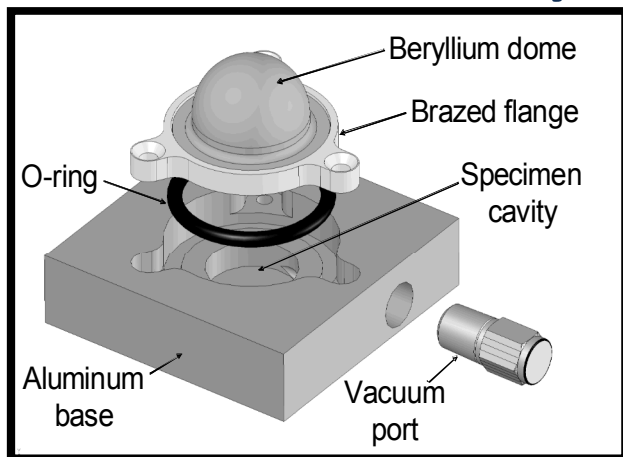


Size Variant Cu NP

- Cu NP samples from 4 separate individuals using HDA and 8N
- Sample preparation
- Processing time
- Addition time
- Dissolution behavior
- Operator discrepancies



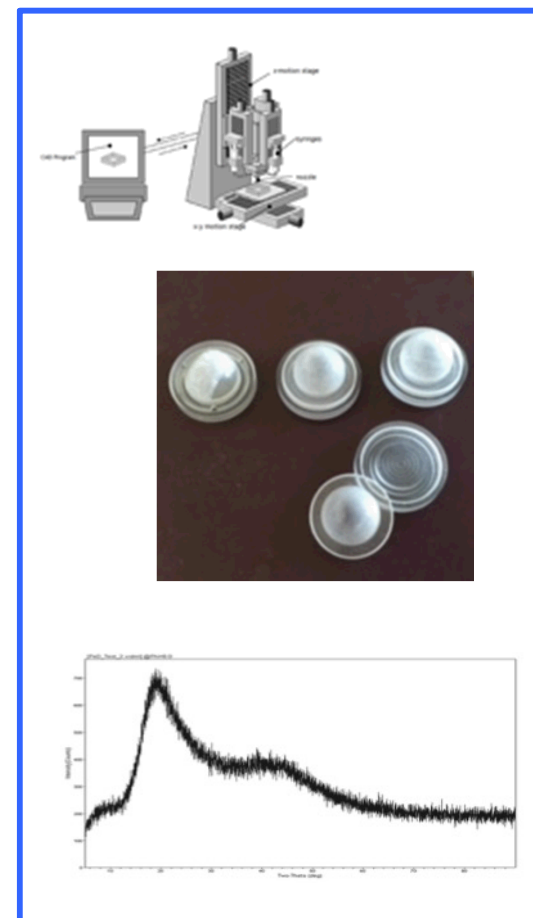
PXRD Analysis



Beryllium Dome
(BeD)
\$10 K



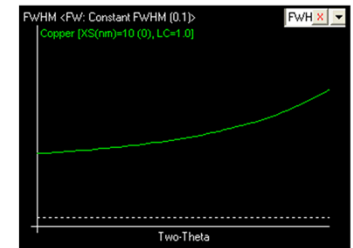
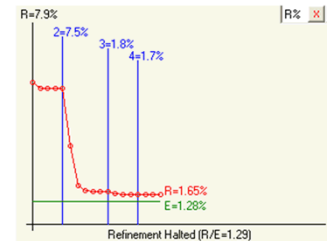
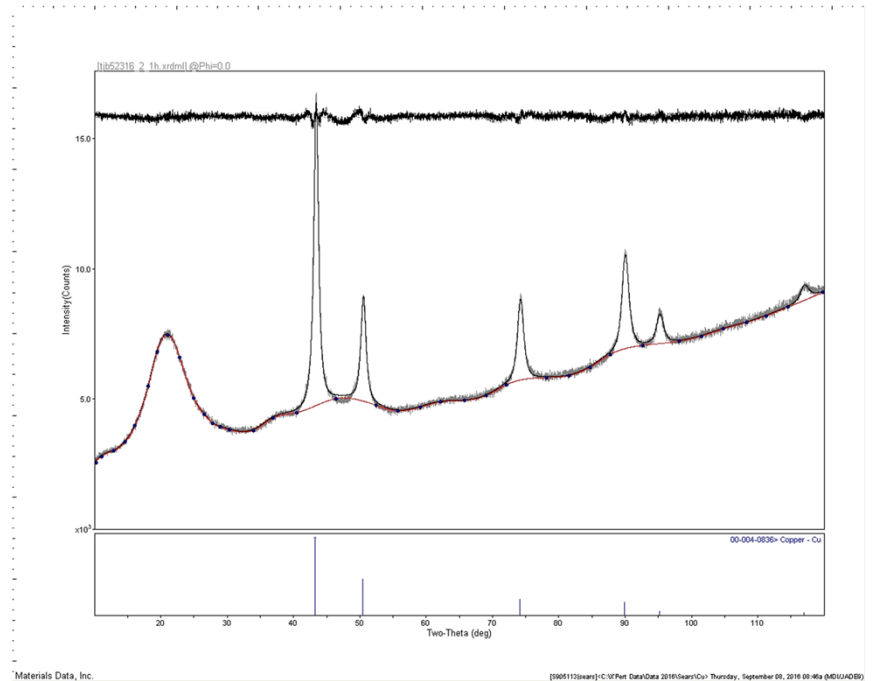
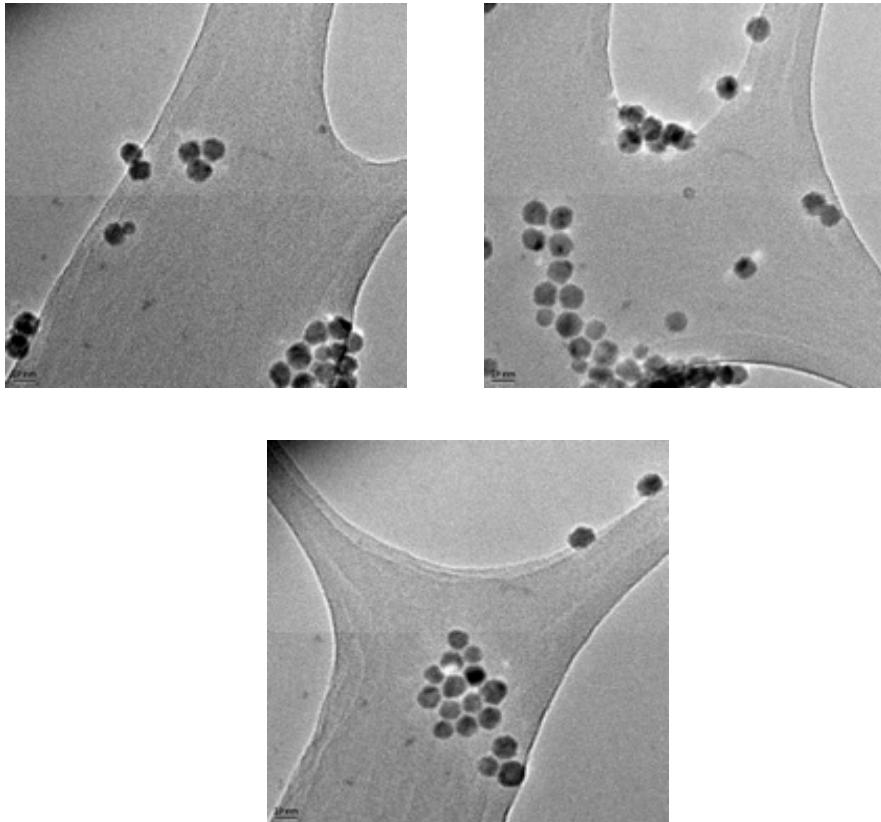
Plastic Dome
(PeD)
\$500



Direct Write PeD
(DW-PeD)
2 for \$80

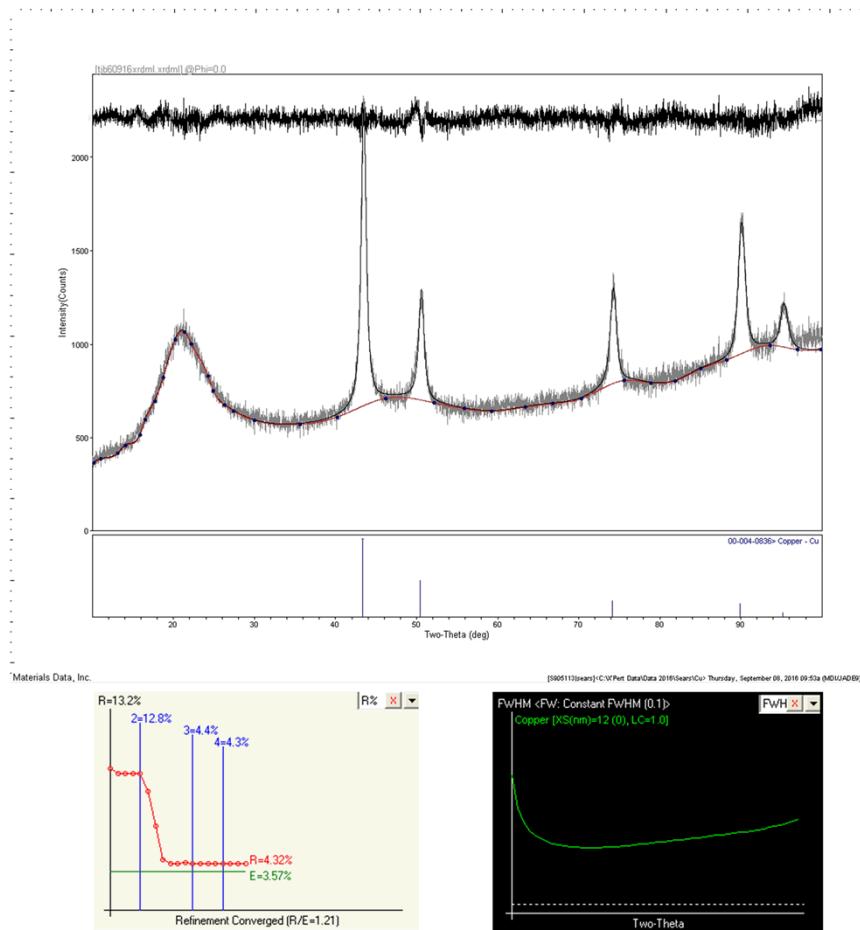
Temperature Reduction

- HDA and 8N route
- Heat and monitor for color changes from yellow solution to a dark red solution
- Observed as early as 150 ° C.



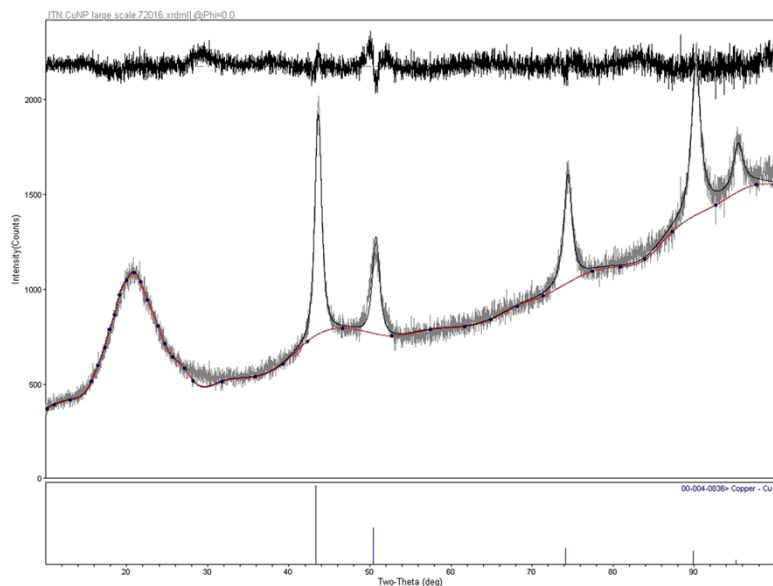
Large Scale, Lower Temperature

- 20 g Cu(Mes) to 180 °C
- Similar results observed



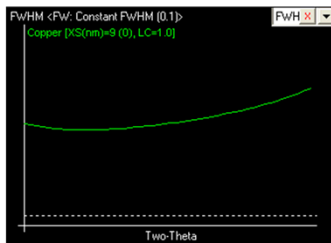
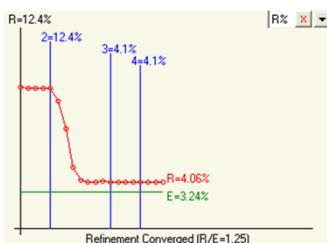
Temporal Study

- 50 g Cu(Mes) Reaction
- Clear defined shape population increased as temperature increased

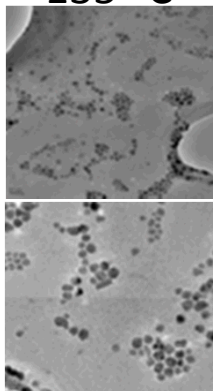


Materials Data, Inc.

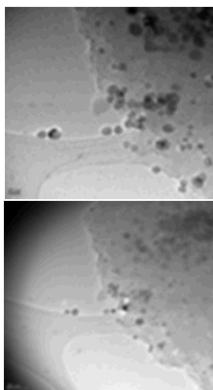
[005113]beam-C:\P\En Data\Ena 2016\Thu- Thursday, September 09, 2016 10:02a (M010408)



135 °C



185 °C



51.6 °C / 29 min



84.2 °C / 40 min



124.6 °C / 1h 12 min



162.2 °C / 1h 41 min



171.1 °C / 2h 21 min

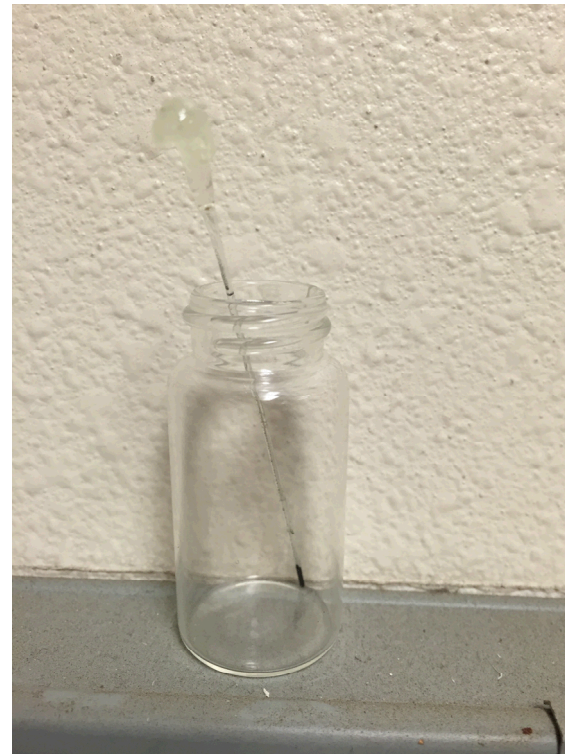
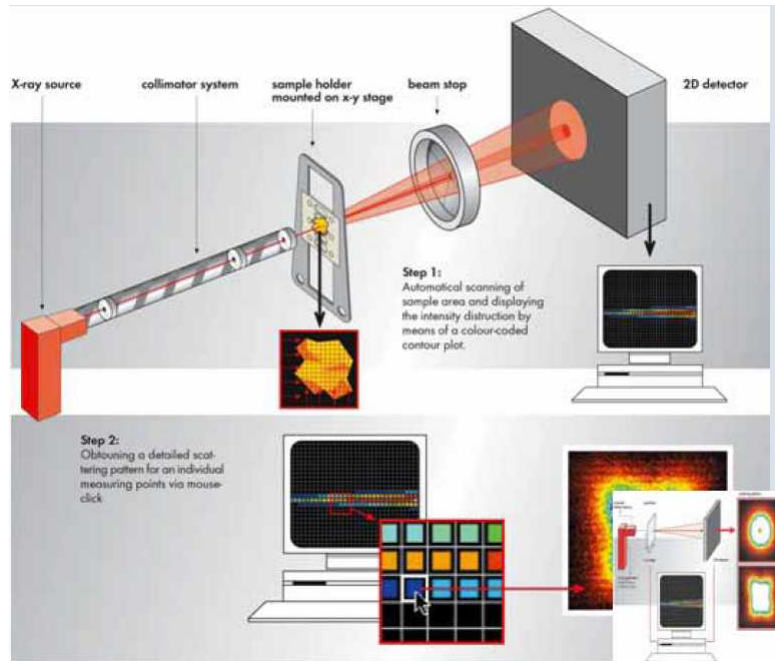


178.4 °C / 2h 29 min



SAXS Introduction

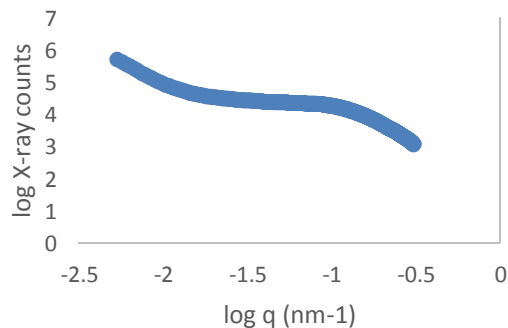
- Small angle X-ray scattering
- Particle shape and size characterization



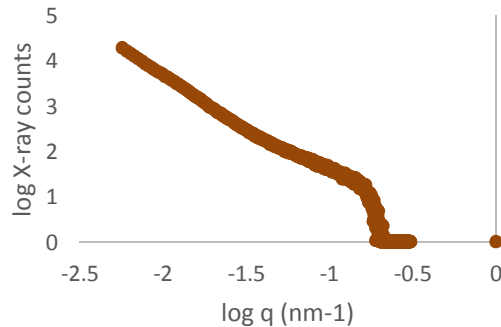
SAXS Characterization

- Distinguishing feature is present as early as 135 °C

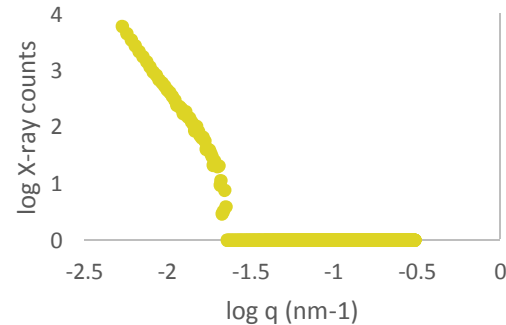
115



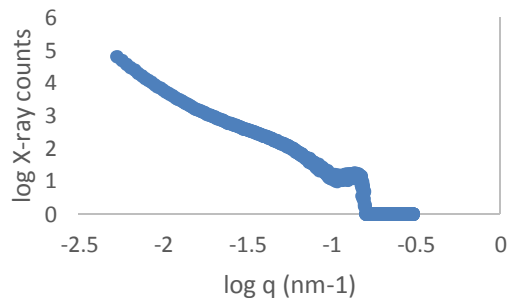
115 red brown



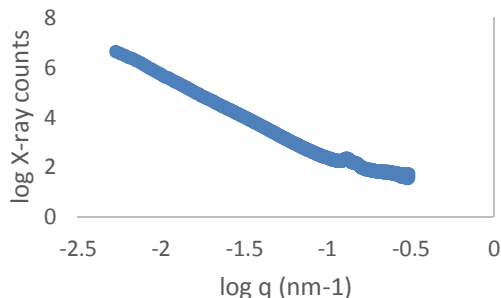
125 yellow



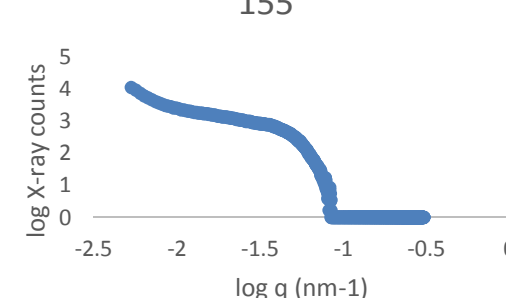
135



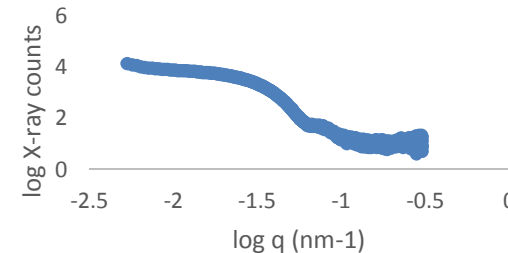
145



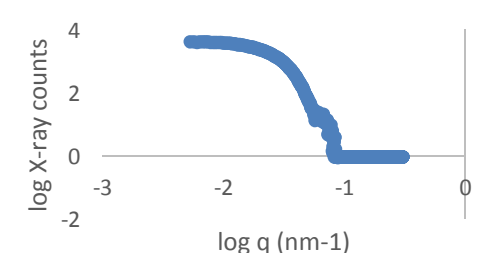
155



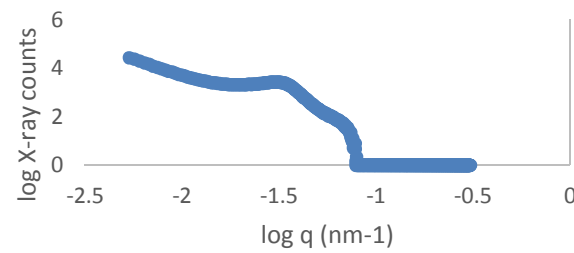
165



175



185

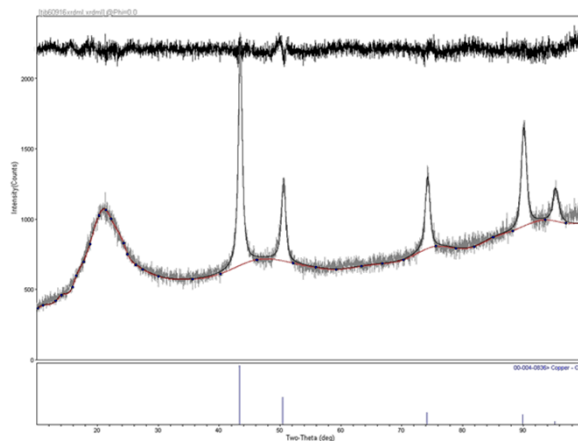
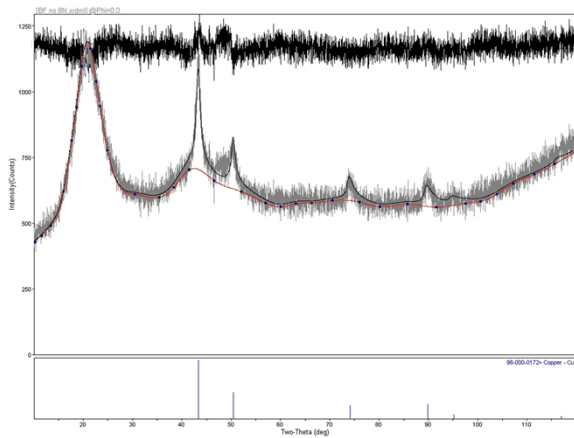


Are You Even Needed, Bro?

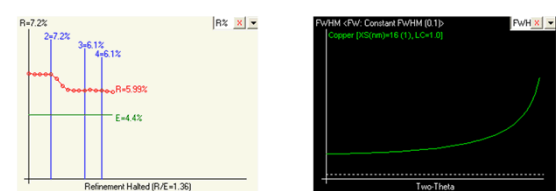
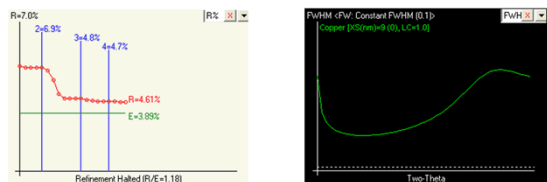
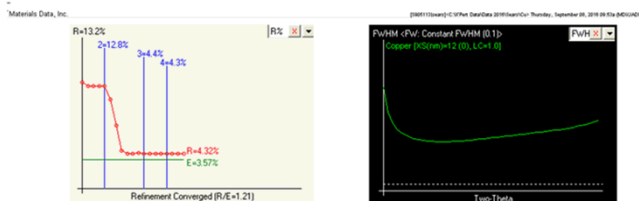
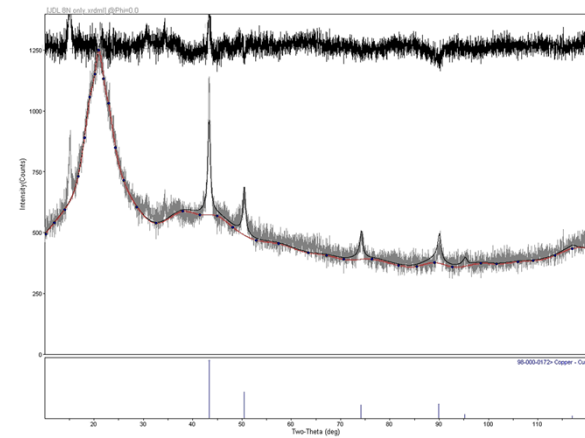
- Cu NP synthesis excluding HDA or 8N from the reaction

8N & HDA

8N-less



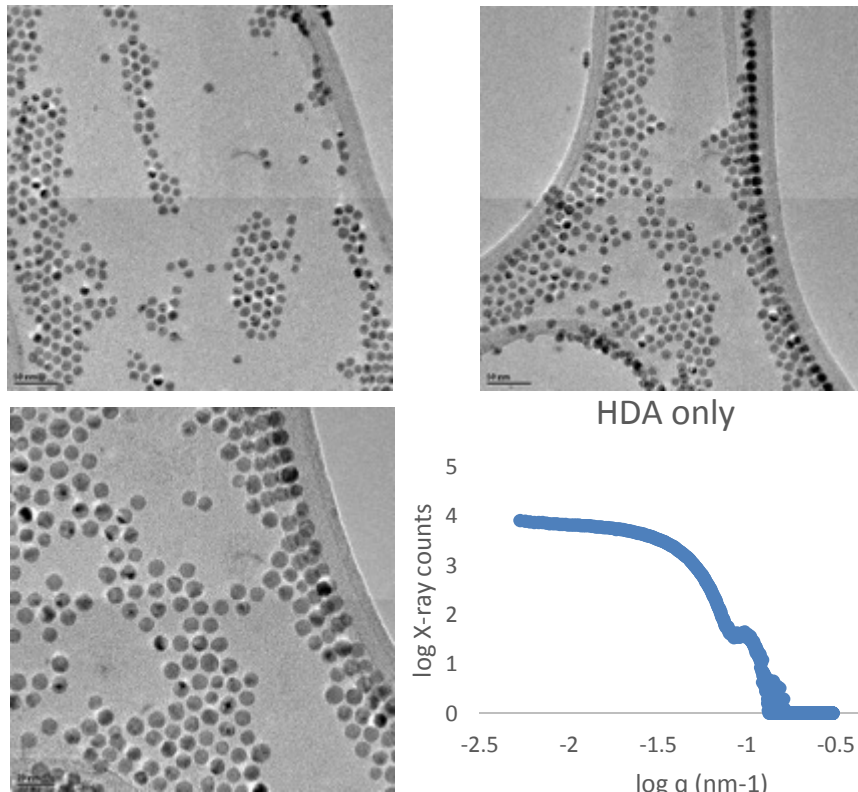
HDA-less



Needed? Cont.

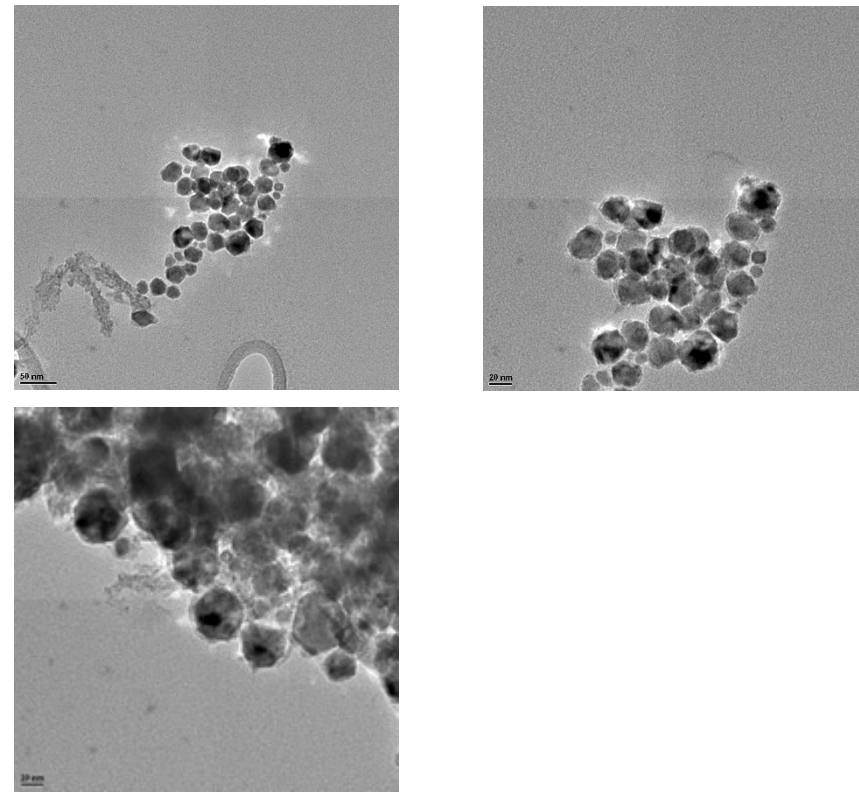
- Cu NP synthesis was successful upon excluding either HDA or 8N from the reaction
- HDA-less route produces larger Cu NP

8N-less

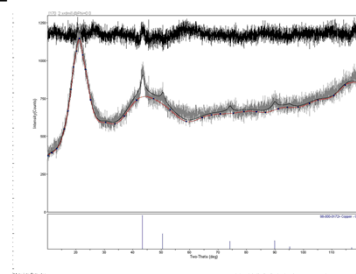
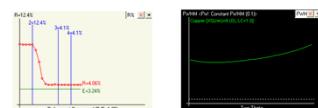
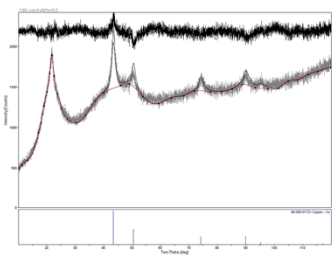


HDA only

HDA-less



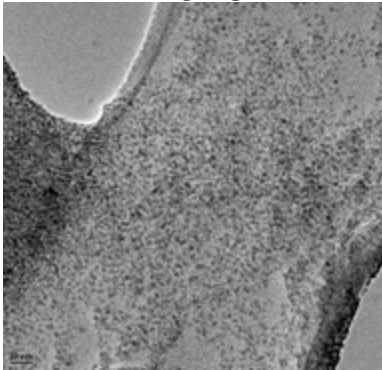
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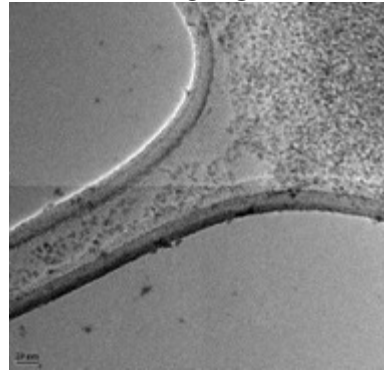
Large Scale 8N-less RXN Cont.

- Small particulates up to 130 °C
- Beyond 130 °C large aggregates are noted that ripen into 8-10 nm Cu NP

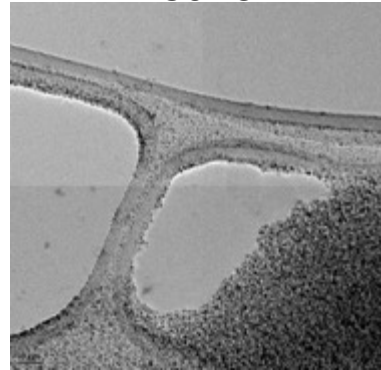
110 °C



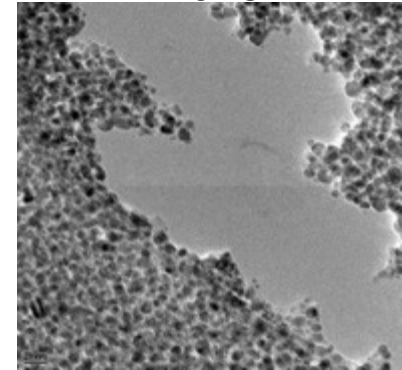
120 °C



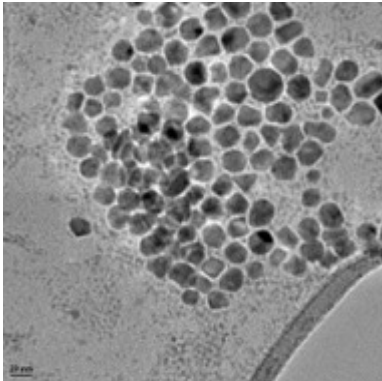
130 °C



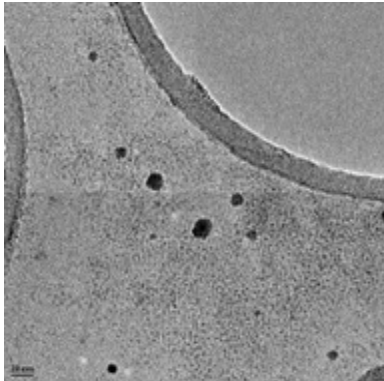
140 °C



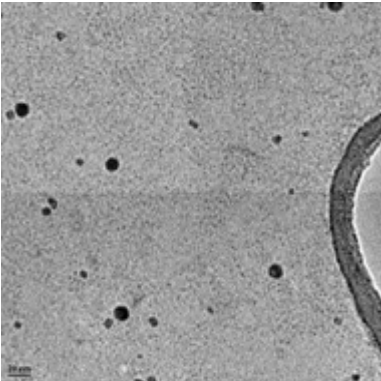
150 °C



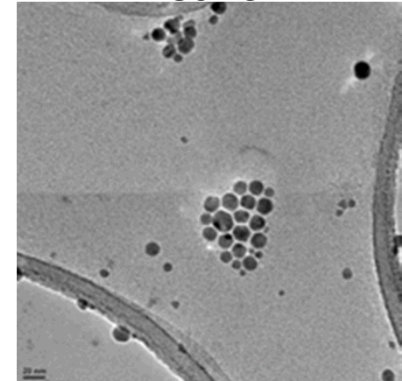
160 °C



170 °C

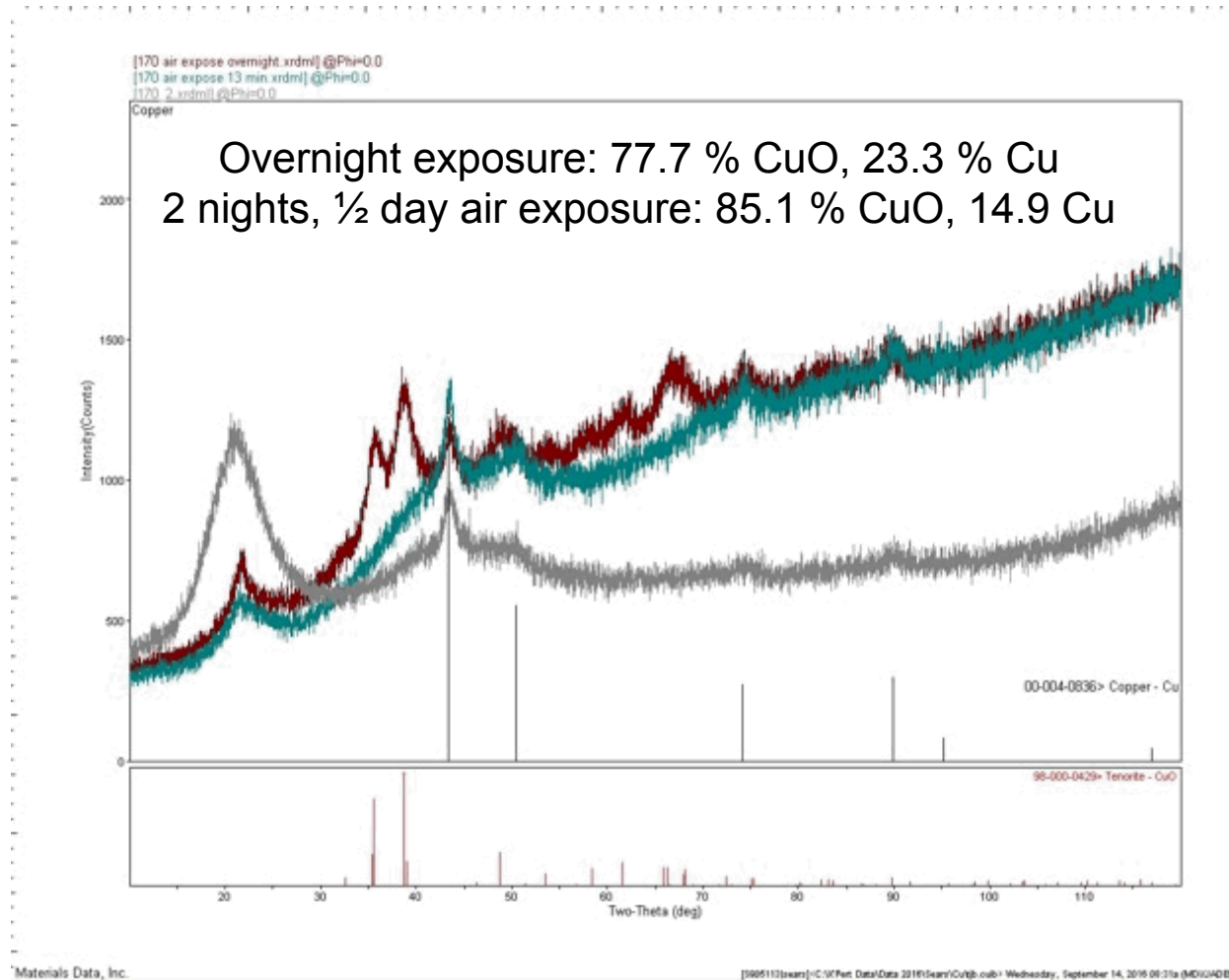


180 °C



Cu NP Oxidation

- Slow oxidation
- CuO observed as early as overnight exposure to air



Conclusions

- Large scale Cu NP generated at lower temperature in a glovebox
- The reaction did not require the presence of both HDA and 8N as validated by TEM, PXRD, and SAXS analysis