# Ink preparation and inkjet printing of eutectic gallium indium nanodroplets

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# Outline

1. Introduction + motivation
2. Ink preparation process and characterization tools
3. Characterizing ethanol-based inks
4. Characterizing ethylene glycol-based inks
5. Preliminary inkjetting experiment

# Introduction to inkjet

- ExFab has a piezo inkjet from Fujifilm Dimatix
- Like your desktop printer, but you bring the ink
- Printer ejects ink droplets
  - Thermal inkjet
  - MEMS piezo inkjet

(Fujifilm)

# Eutectic Gallium Indium (eGaIn)

- eGaIn is a liquid metal, melting point 15.7 °C (liquid at room temperature)
- Mixture 75% Ga, 25% In by mass
- Surface oxide "skin" layer that makes it moldable

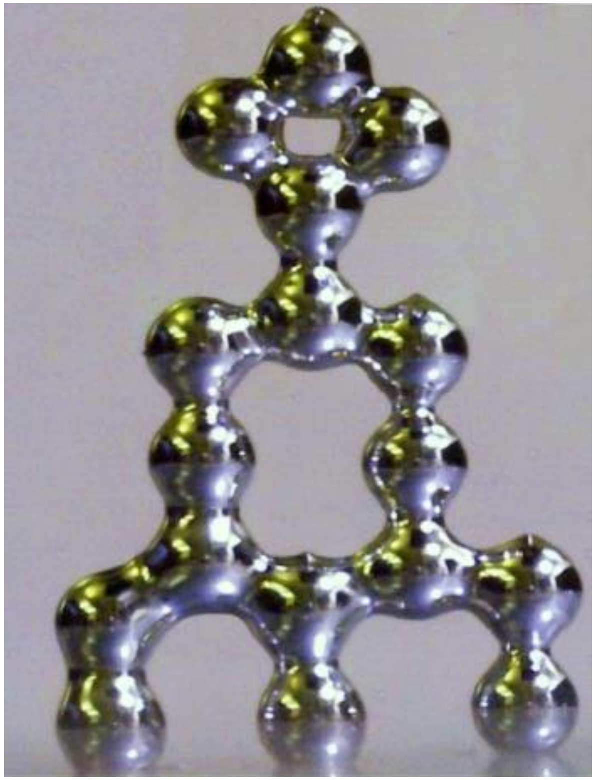
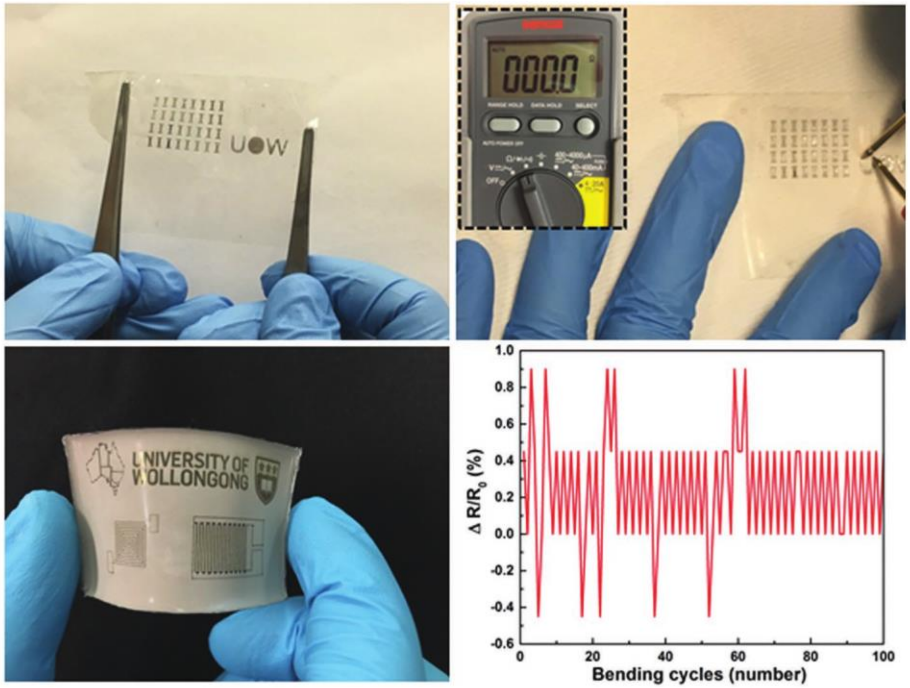
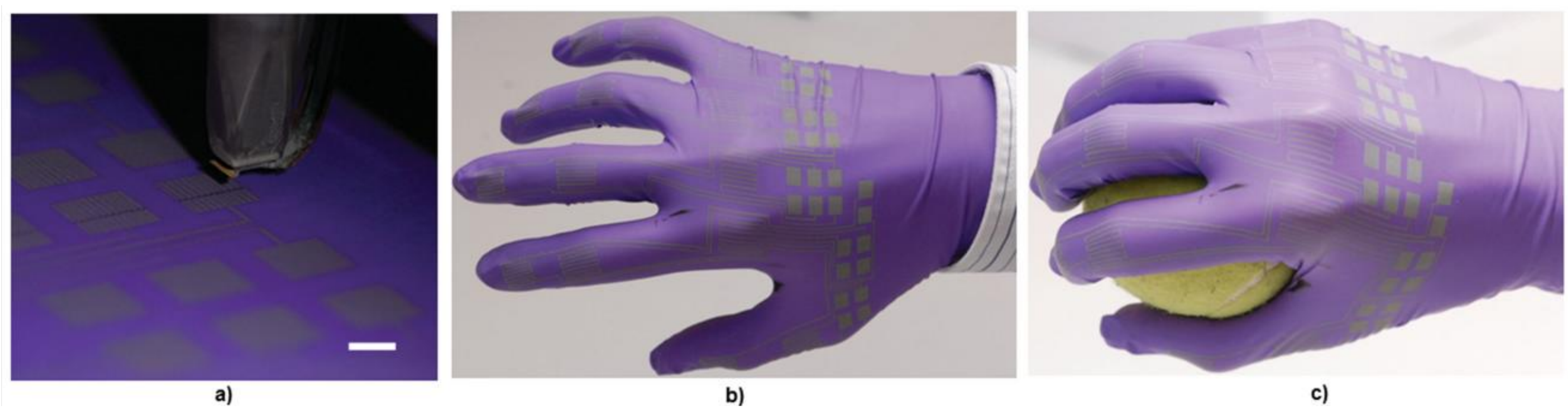


Image from [1] Ladd, C., et all. (2013), 3D Printing of Free Standing Liquid Metal Microstructures. Adv. Mater., 25: 5081–5085. doi:10.1002/adma.201301400

# Goal: Use the Dimatix inkjet to print eGaIn contacts

- Electrical contacts to structures that move or are irregularly shaped
- Conductive patterns for soft or flexible electronics
- Resistivity 2.94 × $10^{-5}$ Ω cm (about 20x bulk copper)



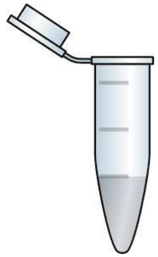




Top: [2] Ren, L., et al. (2016). Adv. Funct. Mater. doi:10.1002/adfm.201603427
Bottom: [3] Boley, J.W., et al. (2015). Advanced Materials 27(14):2355–2360.

# We cannot inkjet arbitrary liquids

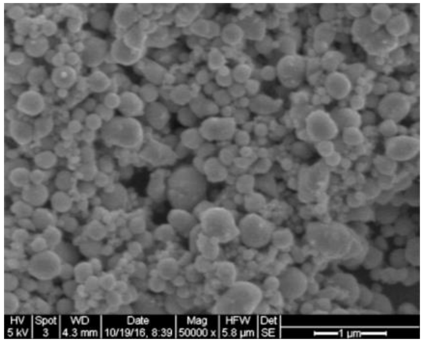
- The ink must satisfy certain properties for printer to form droplets
  - Viscosity $2 < \eta < 30$ cP, ideally $10 < \eta < 12$ cP
  - If using particles, particles << 21.6 μm nozzle diameter
  - Surface tension near 30 dynes/cm
  - No separation or settling
- C**an't directly print bulk** eGaIn, 600 dynes/cm surface tension too high
- Inkjet process development is 90% ink formulation development, 10% printing

# Process flow: print eGaIn like a nanoparticle ink



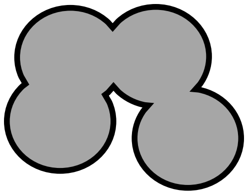
**Mix eGaIn and solvent**

**Divide eGaIn into nanodroplets**




**Filter nanodroplet ink**

**Inkjet print**



**Join droplets**

Images taken (clockwise from upper left) from Clker, Qsonica, Fujifilm

# Ink preparation process and characterization tools

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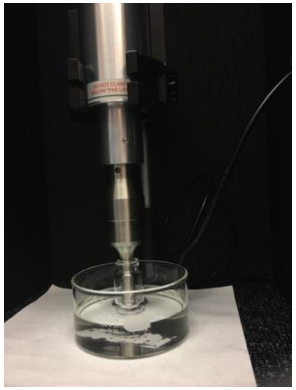
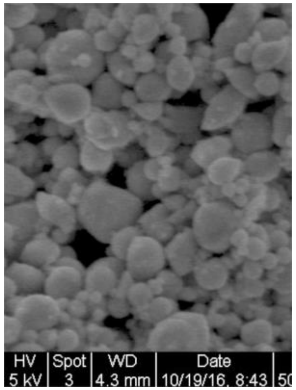
# Ink preparation and characterization (1)



1. Mix ink

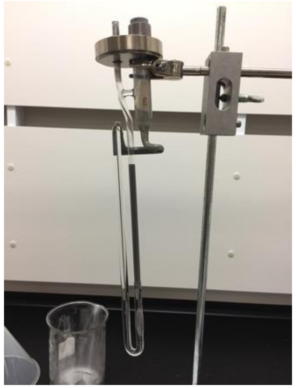
Measure out eGaIn, surfactant, continuous phase solvent and combine. Sonicate for two hours, with water bath for cooling.




2. Drop-cast ink and SEM to measure size distribution

SEM and image processing to quantitatively estimate nanodroplet size distribution, qualitatively estimate nanodroplet density.

# Ink preparation and characterization (2)



3. Measure ink viscosity

Used viscometer and mass balance to calculate ink viscosity. Can also use rheometer in SMF.

4. Settling test to estimate stability

Let sit for 24h to determine whether nanodroplets remain suspended. Settling suggests aggregation (might clog printhead). Ink may also separate in cartridge.

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# Ink preparation and characterization (3)


5. Centrifuge (if needed)

Sediment and remove extremely large particles as a pre-filtration step.

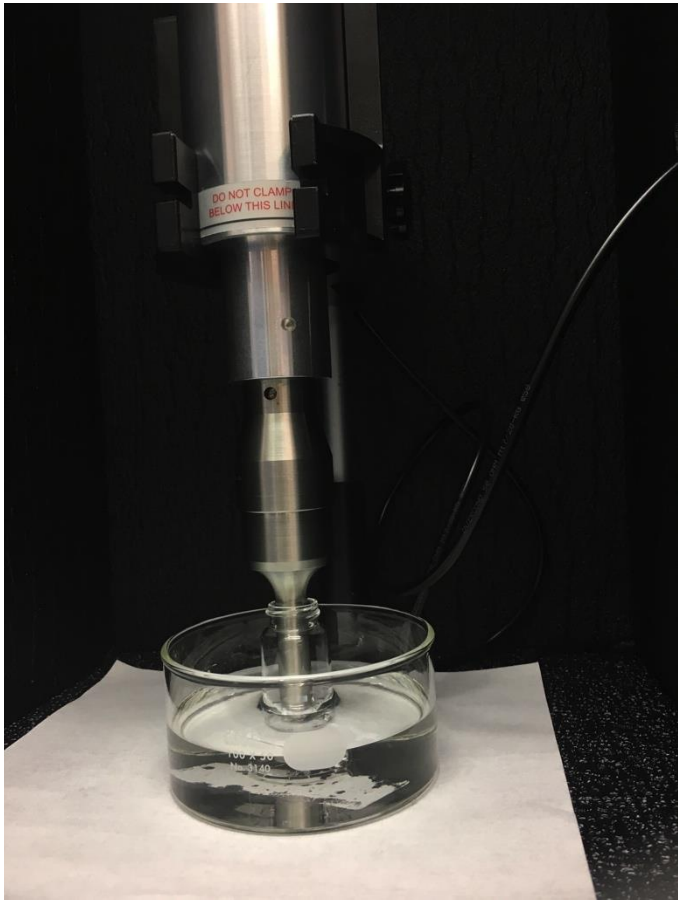
(Fisher)

6. Syringe filter before printing

Filter to remove large particles and clusters that may cause clogging.

# Probe sonication setup in 155 (an ExFab tool!)


Sonicator in soundproof cabinet




Ink preparation. Note water bath for cooling tip/reducing solvent evaporation.

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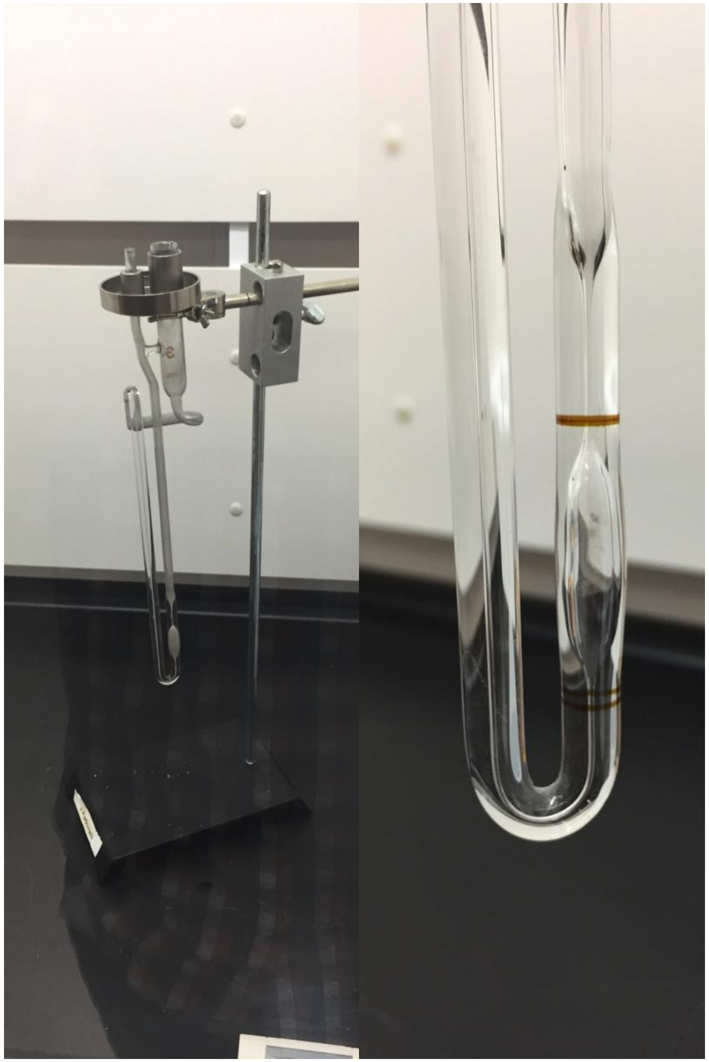
# Capillary viscometer for measuring ink viscosity



- Glass tube with capillary
- To measure:
  1. Measure density of fluid
  2. Time how long it takes for fluid to flow through bulb
  3. Calculate viscosity with calibration constant from manufacturer
- Small (3 mL) sample volume compared to rheometer (10 mL)
- Needs to be dry and clean for accuracy

# Characterizing ethanol-based inks (what a bad ink looks like)

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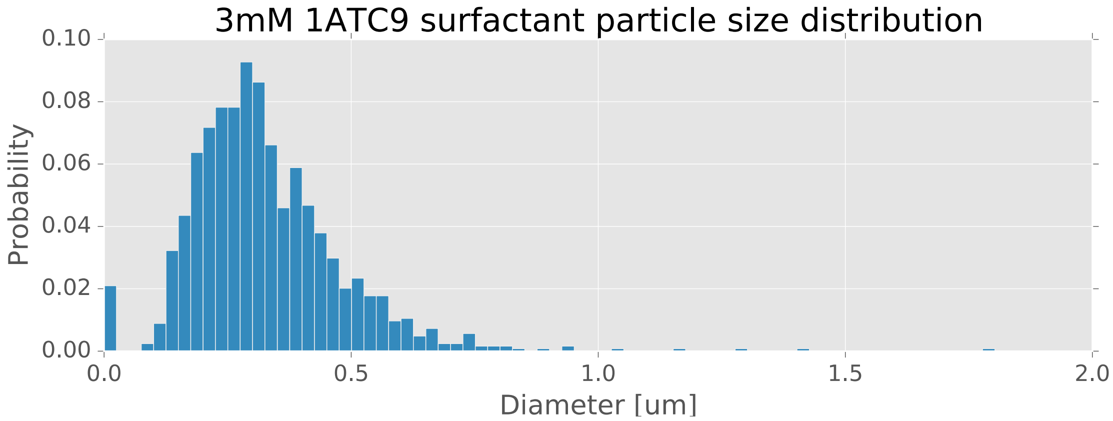
# Ethanol-based ink experiments

- Ink formulation from [3] with correspondence from authors
  - 90 mg/mL eGaIn to ethanol, 3 mM of thiol SAM surfactants 3-mercapto-n-nonylproprionamide (1ATC9) or 1-dodecanethiol (C12)
- Surfactant serves as surface passivation
  - Slows oxidation at surface, tighter size distributions

a) b) c)

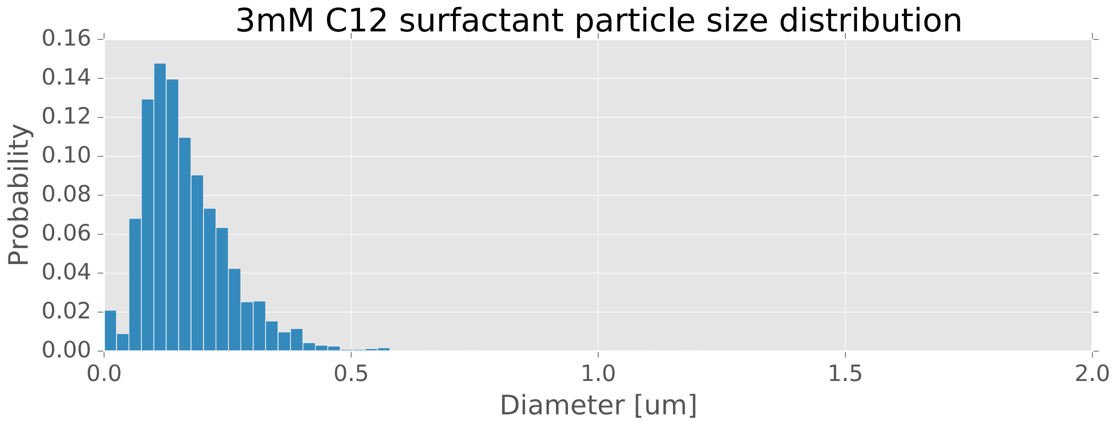
[3] Boley, J.W., et al. (2015). Advanced Materials 27(14):2355–2360.

# Ethanol ink particle sizes are printable



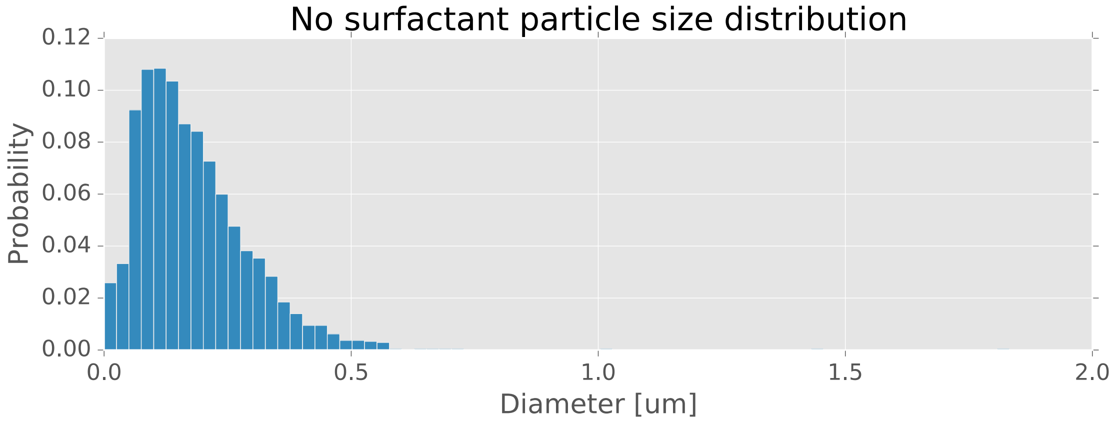

**3 mM 1ATC9, 90 mg/mL eGaIn:**

302 nm median diam.
334 nm mean diam.




**3 mM C12, 90 mg/mL eGaIn:**

147 nm median diam.
170 nm mean diam.




**No surfactant, 90 mg/mL eGaIn:**

157 nm median diam.
184 nm mean diam.

# Ethanol ink viscosities are too low to print

| Ink Formulation | Flow time [s] | Kinematic viscosity [cSt] | Density [g/mL] | Viscosity [cP] |
|---|---|---|---|---|
| **ethanol** (sanity check) | 44 | 1.4 | 0.82 | **1.1** Ref. values [1] 1.144 mPa s @ 20°C 1.040 mPa s @ 25°C |
| **ethanol, 3 mM 1ATC9, 90 mg/mL eGaIn (1)** | 61 | 1.9 | 0.88 | **1.6** |
| **ethanol, 3 mM C12, 90 mg/mL eGaIn** | 41 | 1.3 | 0.90 | **1.1** |
| **ethanol, 90 mg/mL eGaIn** | 41* | 1.3 | 0.90 | **1.1** |
| **ethanol, 3 mM 1ATC9, 90 mg/mL eGaIn (2)** | 40* | 1.2 | 0.93 | **1.1** |

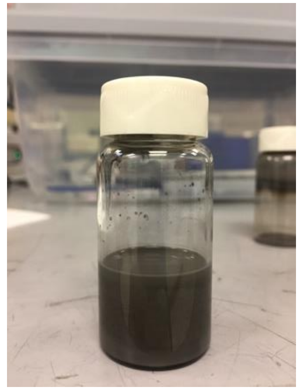
**Printable range is 2-30 cP, ideal range 10-12 cP**

* Likely inaccurate, ink separated in viscometer while measuring

[1] http://www.cheric.org/research/kdb/hcprop/cmpsrch.php

# Ethanol inks are not consistently stable

**3 mM 1ATC9, 90 mg/mL eGaIn solution**

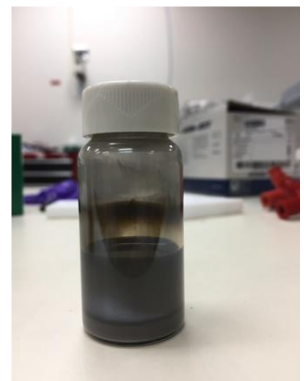


24h

**Complete separation**

**3 mM 1ATC9, 90 mg/mL eGaIn solution**

24h

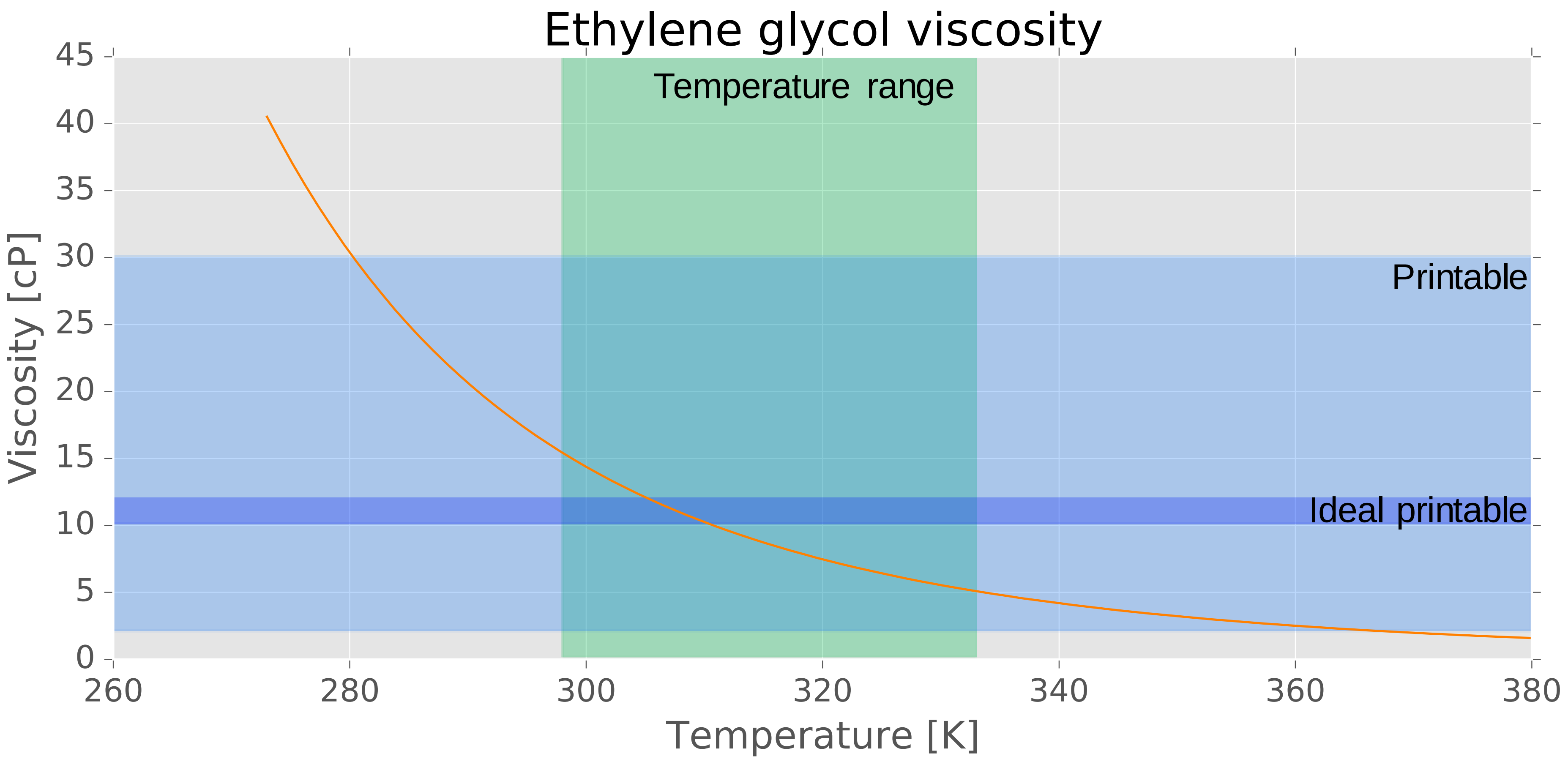


**Still suspended**

- Settling makes printing difficult and nonuniform
- Could be a sign of particle aggregation and clogging
- Given that the viscosities are too low, not worth solving

# Moving to a higher viscosity continuous phase ink

# Ethylene glycol as the ink continuous phase




- Can use temperature to control ink viscosity
- Higher viscosity makes it easier for ink to stay suspended

[1] http://www.cheric.org/research/kdb/hcprop/cmpsrch.php

# The ink viscosities are printable at room temperature

| Ink Formulation | Flow time [s] | Room temperature kinematic viscosity [cSt] | Density [g/mL] | Room temperature viscosity [cP] |
|---|---|---|---|---|
| **ethylene glycol** (sanity check) | 466 | 14.3 | 1.16 | **16.6**<br>18.365 @ 20°C [1]<br>15.128 @ 25°C [1] |
| **ethylene glycol, 90 mg/mL eGaIn, no surfactant** | 508 | 15.6 | 1.18 | **18.4** |
| **ethylene glycol, 90 mg/mL eGaIn, 1 mM C12** | 443 | 13.6 | 1.22 | **16.6** |
| **ethylene glycol, 90 mg/mL eGaIn, 3 mM C12** | 381 | 11.7 | 1.24 | **14.5** |

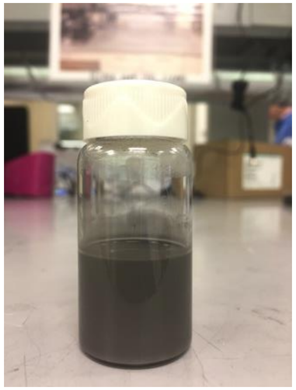
**Printable range is 2-30 cP, ideal range between 10-12 cP**

(We can use raise ink temperature to lower viscosity during printing)

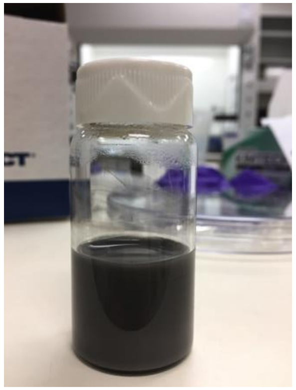
[1] http://www.cheric.org/research/kdb/hcprop/cmpsrch.php

# Ethylene glycol inks are stable

**ethylene glycol 90 mg/mL eGaIn, no surfactant:**



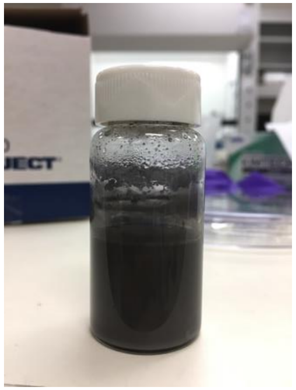
12h



**Still suspended**

**ethylene glycol,90 mg/mL eGaIn, 1 mM C12:**

12h



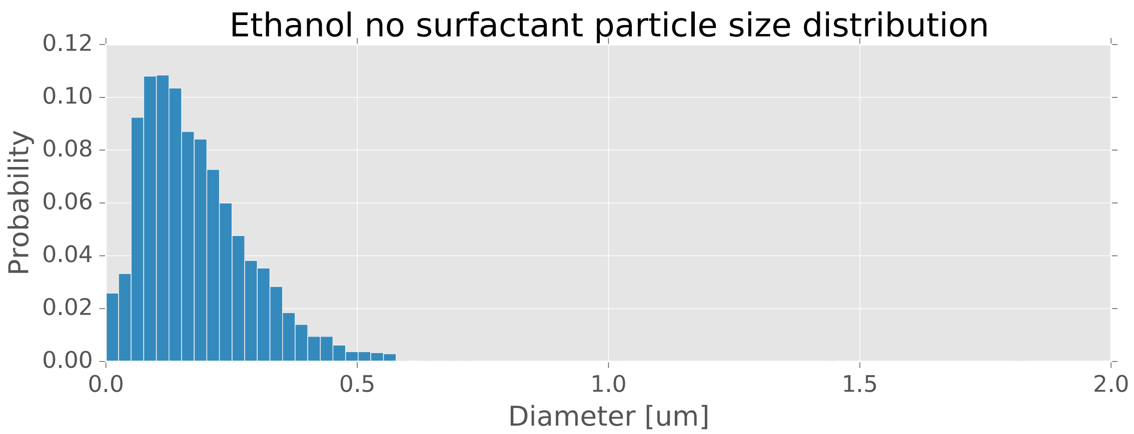
**Still suspended**

**ethylene glycol, 90 mg/mL eGaIn, 3 mM C12:**

12h

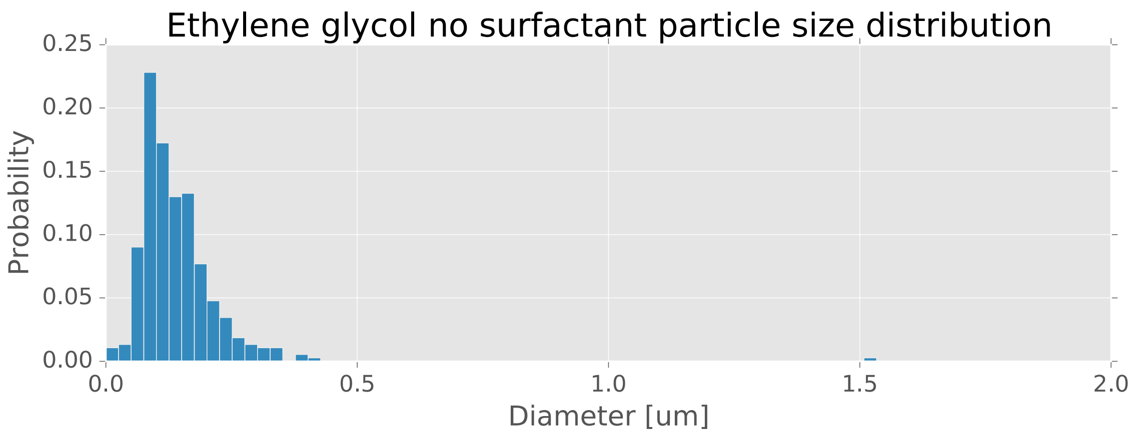
**Still suspended**

# Particle sizes are comparable to ethanol inks




**Ethanol, no surfactant, 90 mg/mL eGaIn:**

157 nm median diam.
184 nm mean diam.



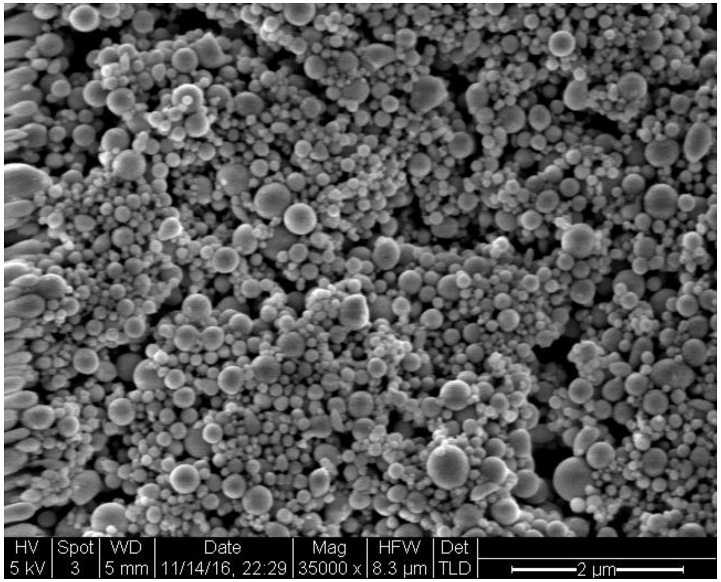

**Ethylene glycol, no surfactant, 90 mg/mL eGaIn:**

125 nm median diam.
142nm mean diam.

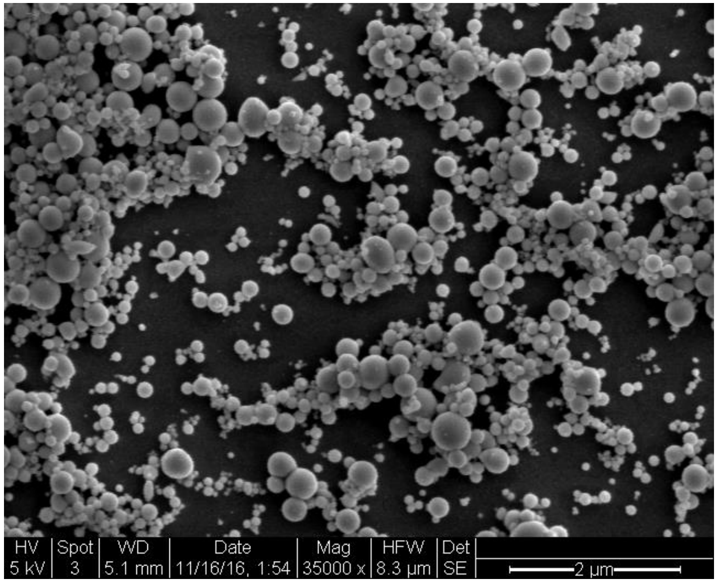
Particle size distribution relatively tight and in the correct range, surfactant doesn't appear necessary

# Filtering the ink to prevent clogging the printhead

# eGaIn particles are difficult to syringe filter



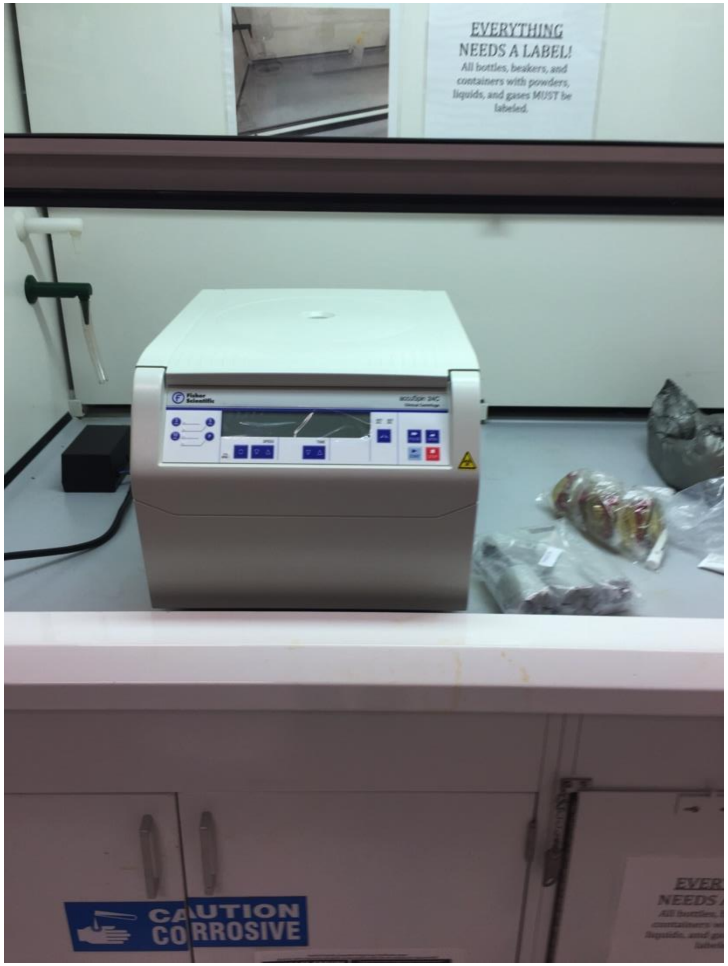

Before syringe filter




After 1µm syringe filter

- 1µm filter clogs
  - Particle density drops
  - Ink no longer uniform, sometimes even settles
  - Ink volume limited to ~1 mL, want closer to ~10 mL
- Need to remove debris and large particles without fine filter

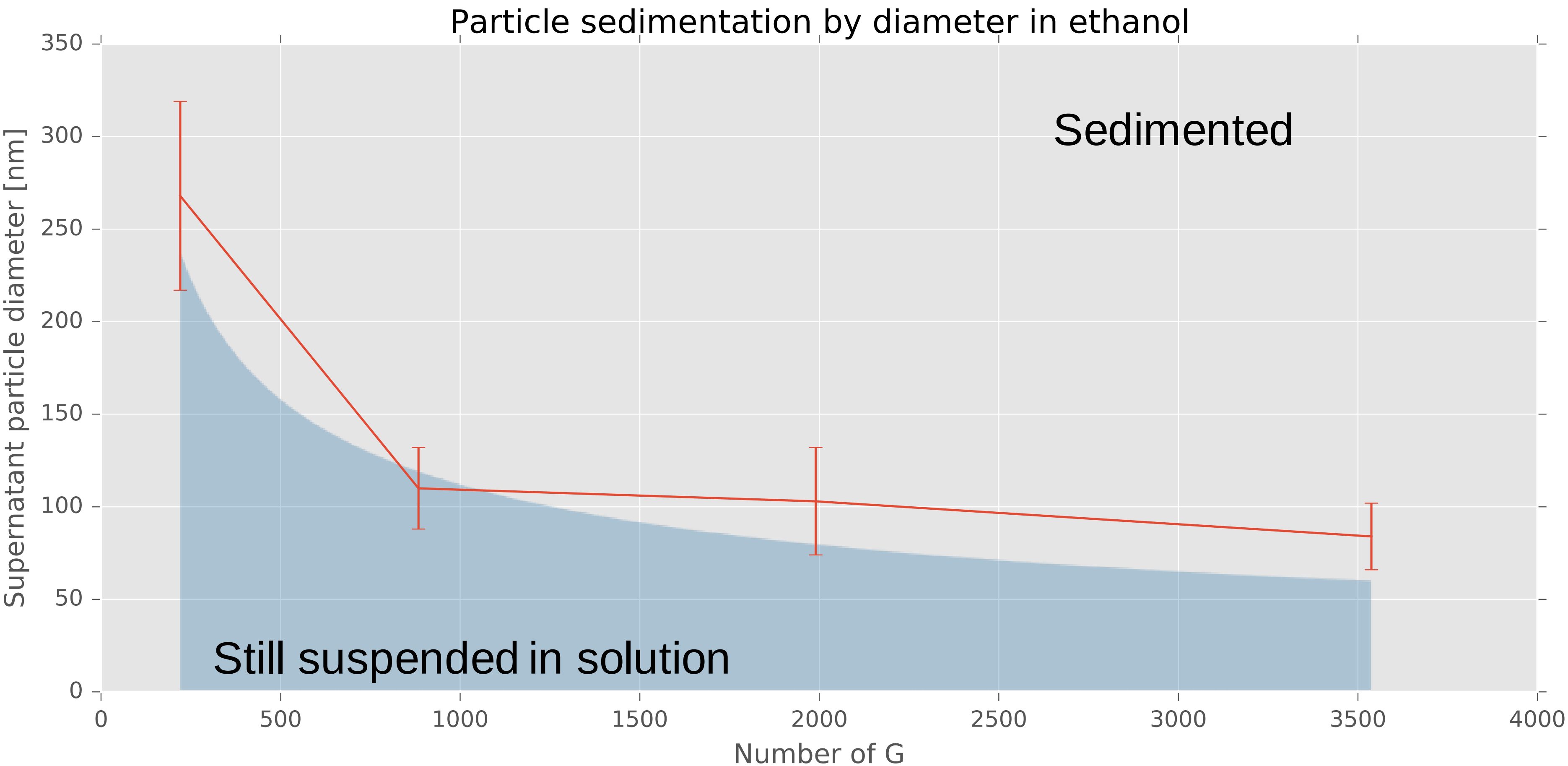
# Using centrifugation to select for particle size




Low speed centrifugation + coarse filtration instead of fine filtration

(also an ExFab tool!)

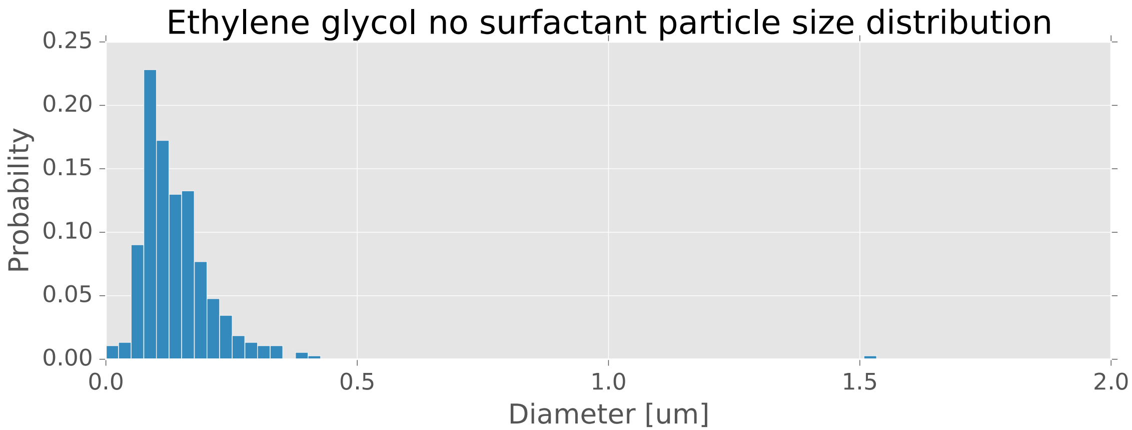
# We can a priori estimate how much centrifugation is needed




Stoke’s law estimates fit reasonably to eGaIn particle differential segregation from [1] (guessed parameters)

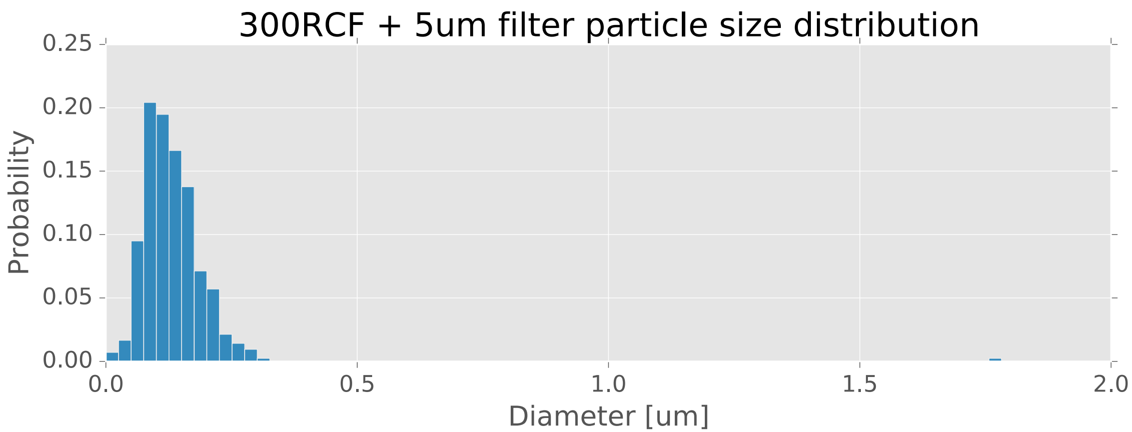
[1] Boley, J. W., *et al*. Hybrid Self-Assembly during Evaporation Enables Drop-on-Demand Thin Film Devices. ACS Appl. Mater. Interfaces (2016). doi:10.1021/acsami.5b12687

# Centrifuge + coarse filtration narrows size distribution




**Ethylene glycol, no surfactant, 90 mg/mL eGaIn:**

125 nm median diam.
142nm mean diam.

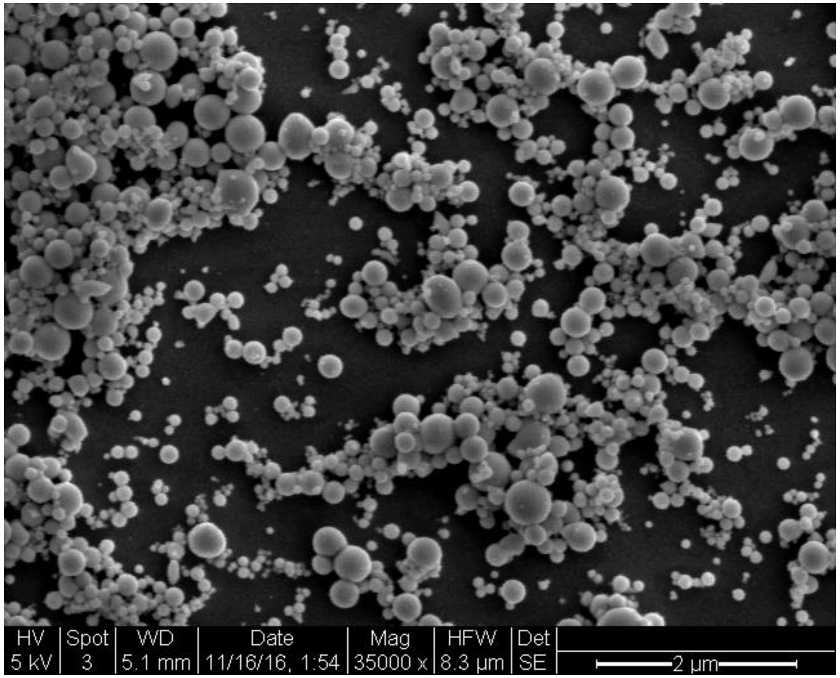



**Ethylene glycol, no surfactant, 90 mg/mL eGaIn, 300 RCF and 5 µm** filter**:**

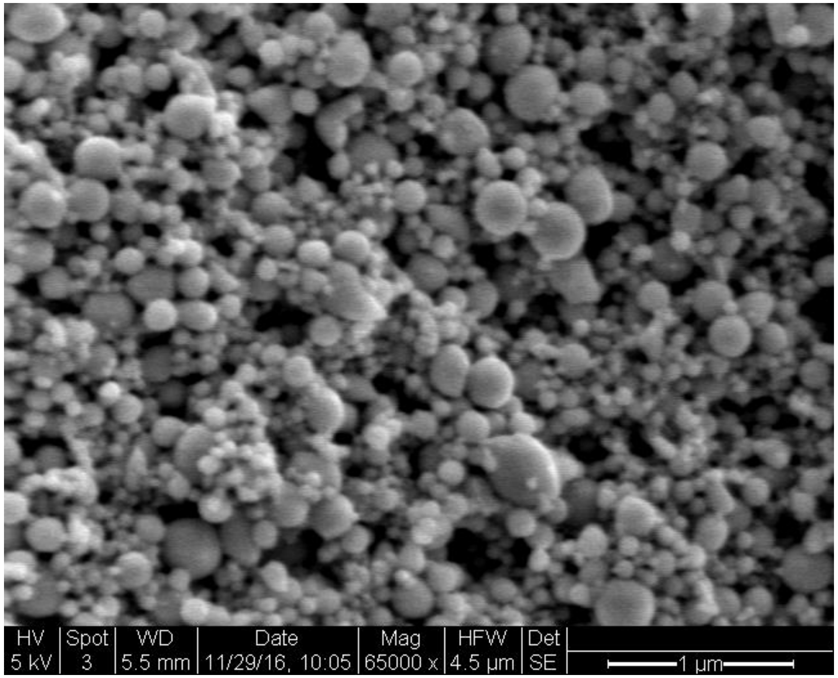
123 nm median diam.
134 nm mean diam.

Centrifuged at 300 RCF, which should sediment all particles larger than 1.6 µm according to modeling

# The particle density is much higher than with 1µm filtration




Ethylene glycol, no surfactant, 90 mg/mL eGaIn after 1µm syringe filter

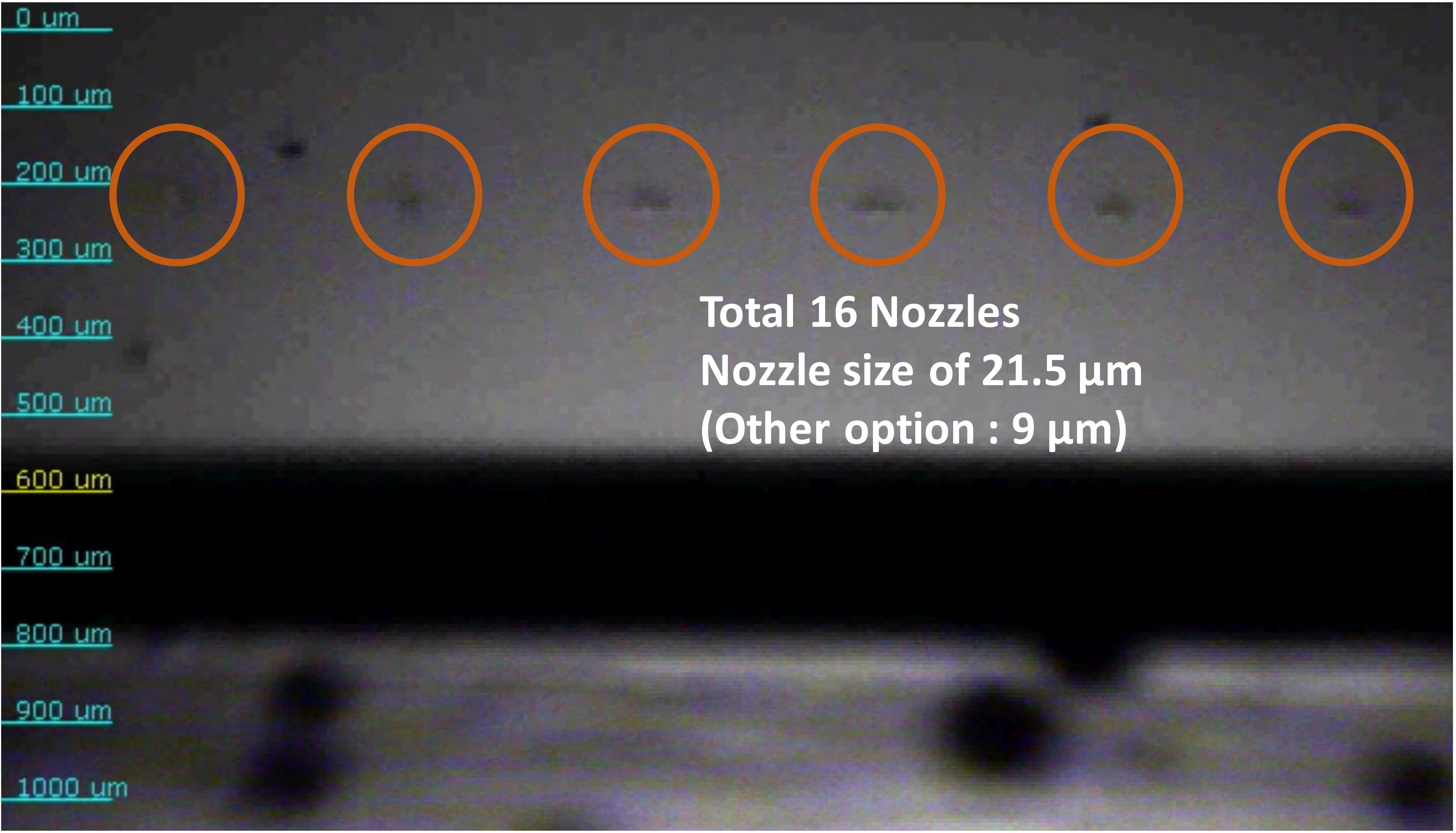



Ethylene glycol, no surfactant, 90 mg/mL eGaIn after centrifuge and 5µm filter

Centrifugation also lets us prepare 10 mL ink at a time

# (Preliminary) Inkjet Test

# Printing Test

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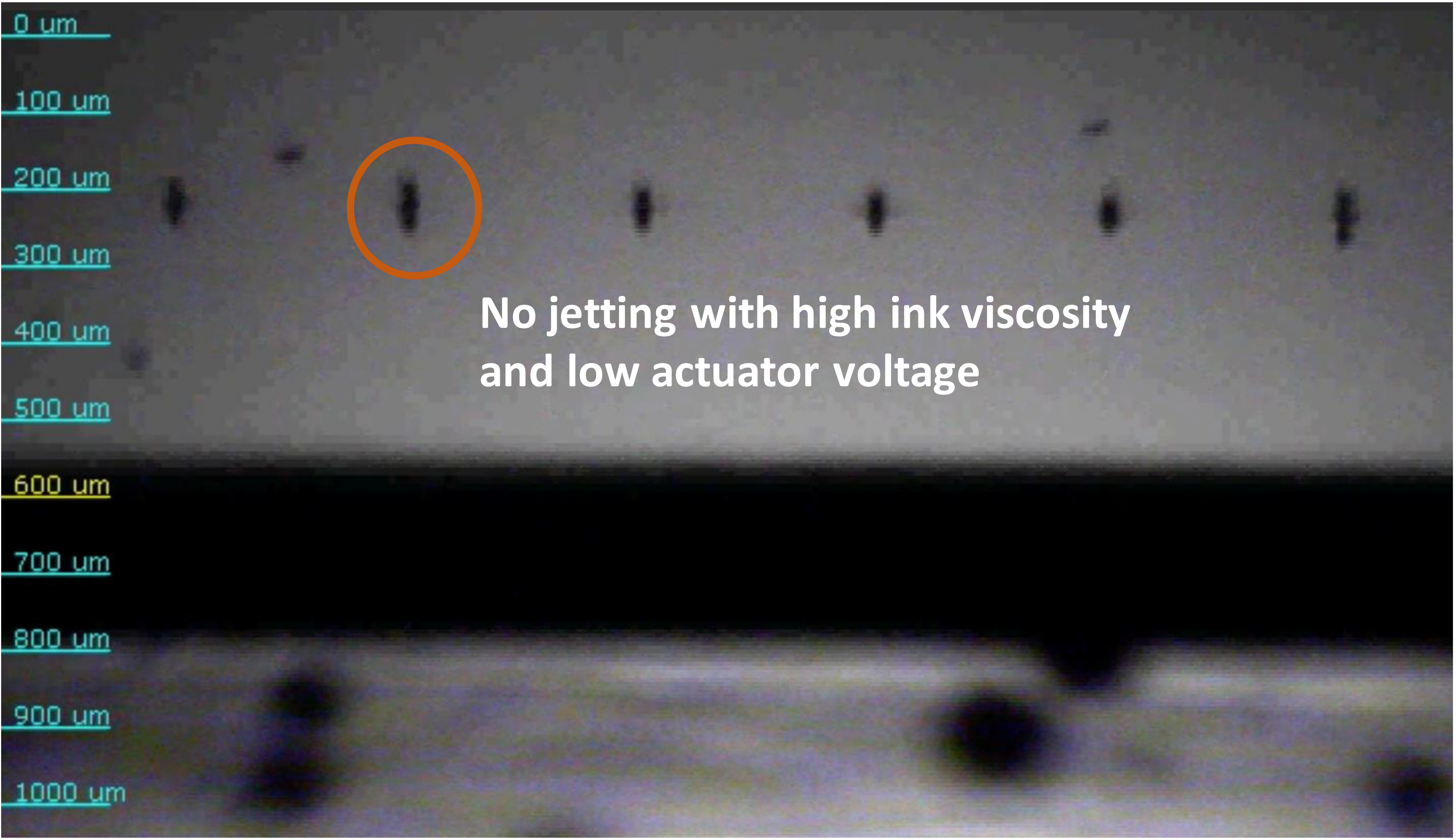
# Printing Test

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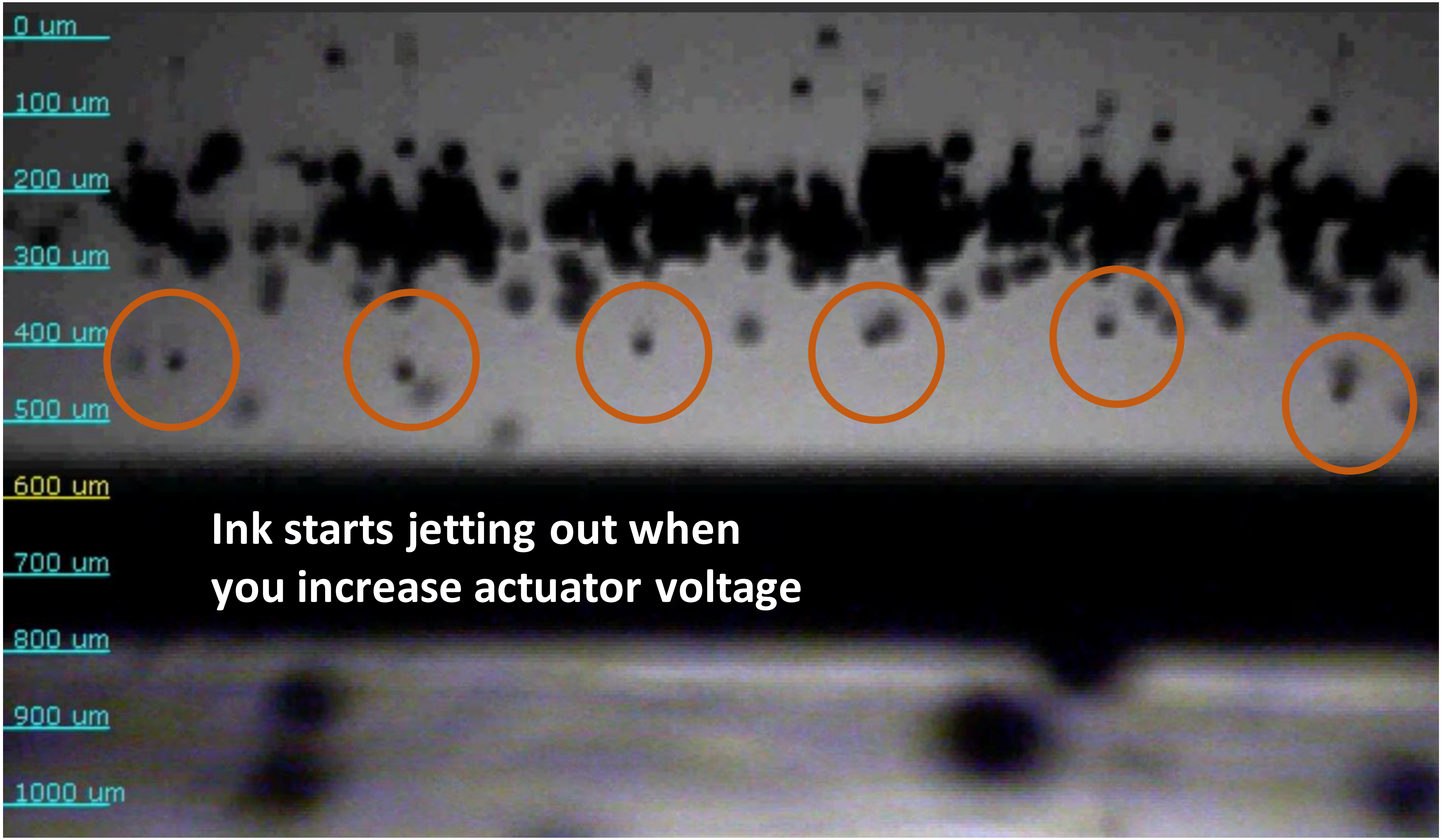
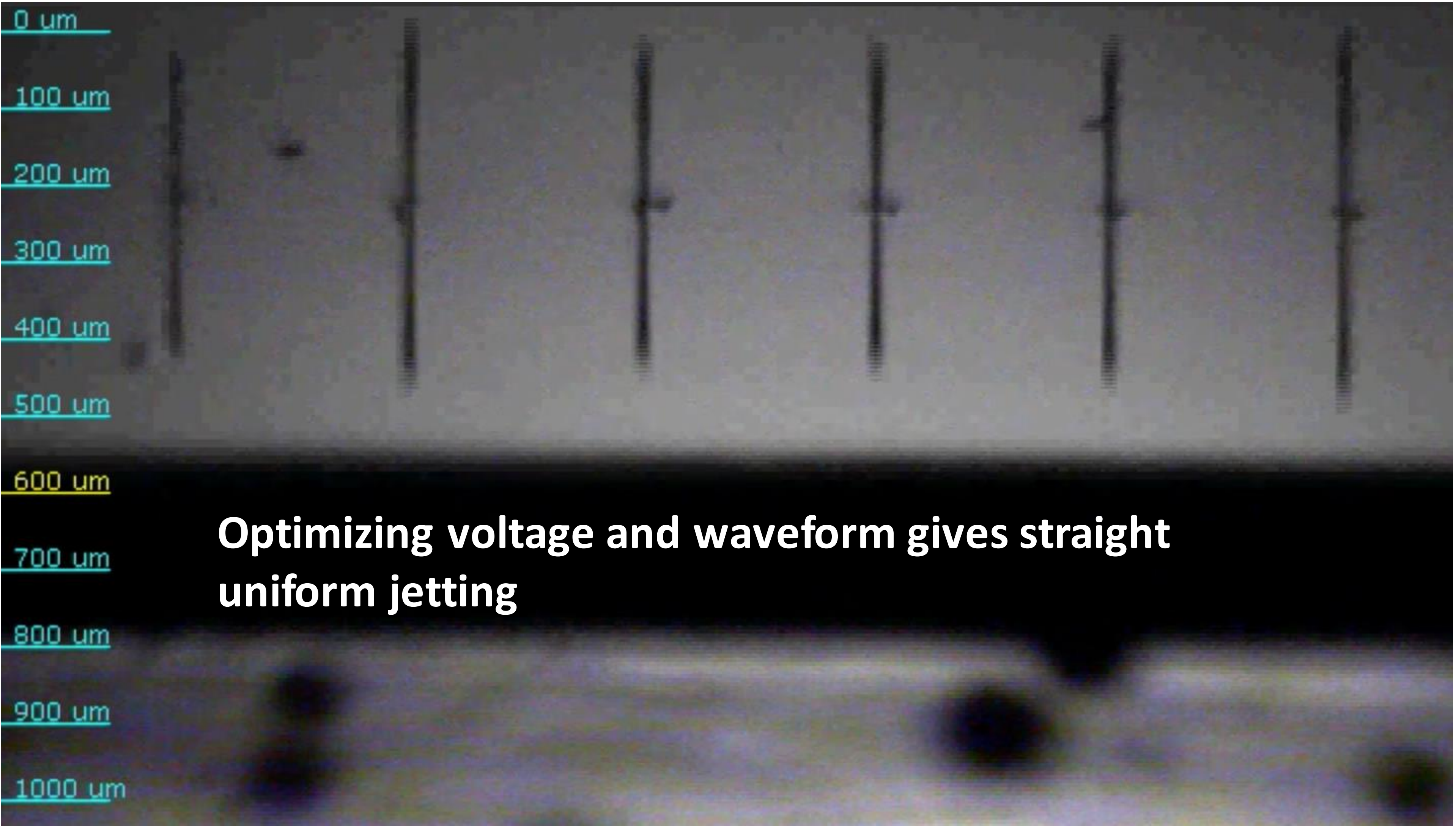
# Printing Test



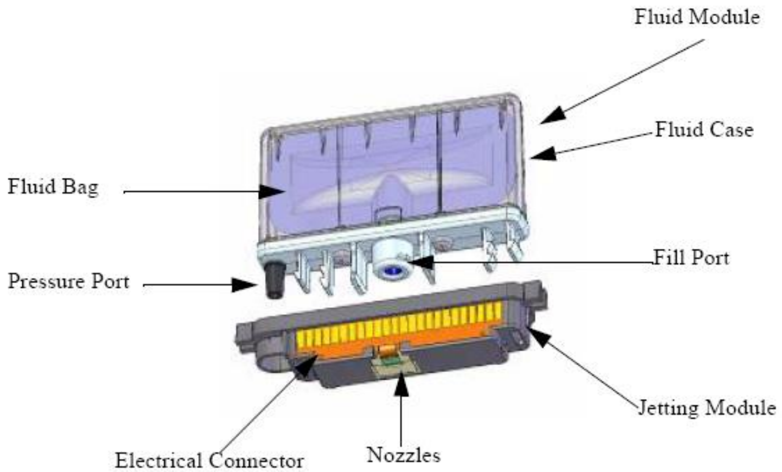
# Printing Test

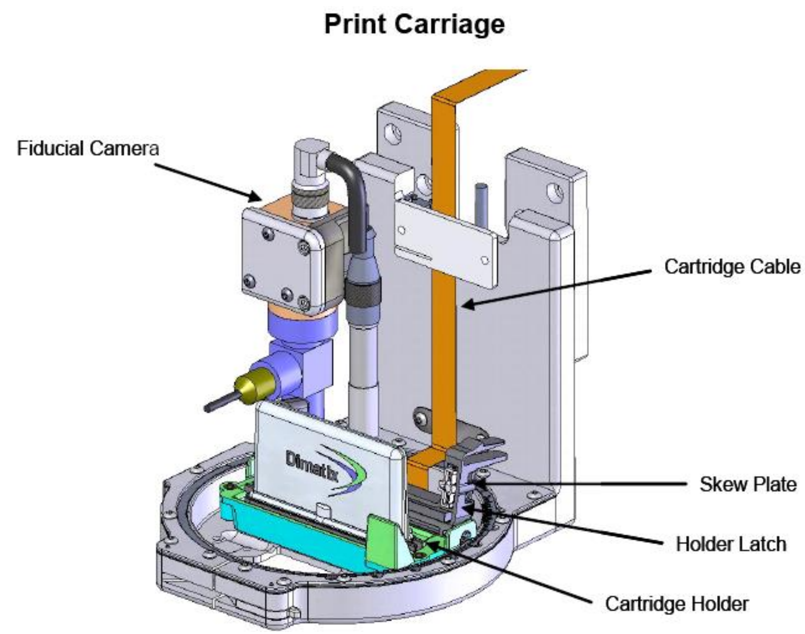


# Conclusions

- Developed techniques for ink processing with probe sonicator and centrifuge
- Explained how to characterize ink
- Found ink formulation for inkjet printing eGaIn with ethylene glycol continuous phase
- Jetting experiment shows that ink is printable
- Next steps:
  - Pattern eGaIn with printer
  - Explore droplet joining techniques

# Print cartridge and setup



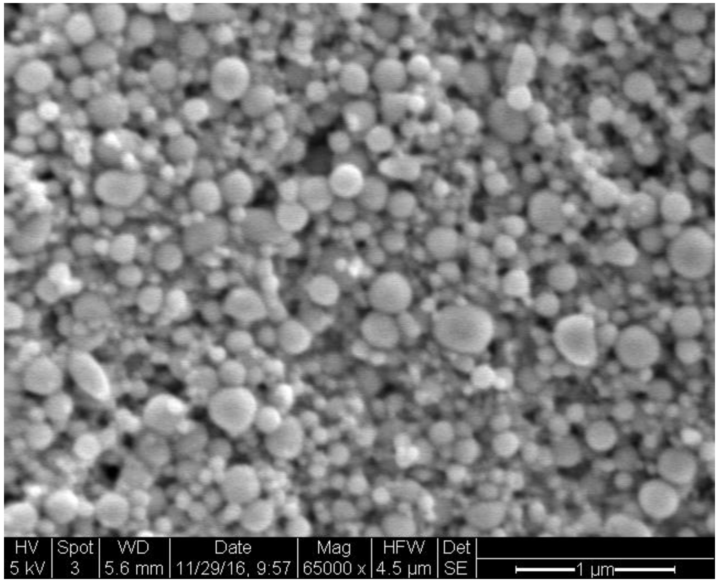



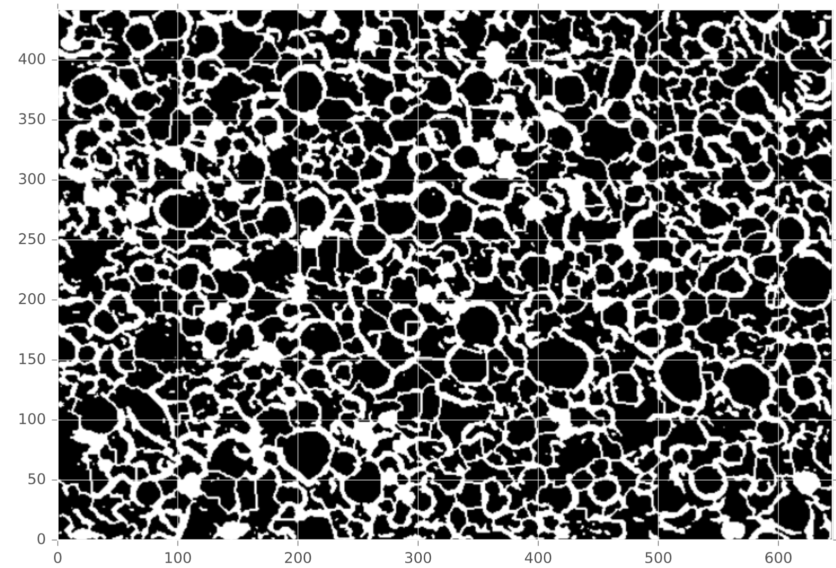

- Filteration is used before loading the ink to the cartridge.
- Degassing is important to have a proper jetting.
- Fiducial Camera is useful for jetting condition control.

# Why inkjet printing?

- Patterning without expensive tools
- No cleanroom!
- Maskless
- Applicable on various substrates
- Less wasteful of materials
- Film quality is relatively controllable
- Processed in air at room temperature
- Industry compatible

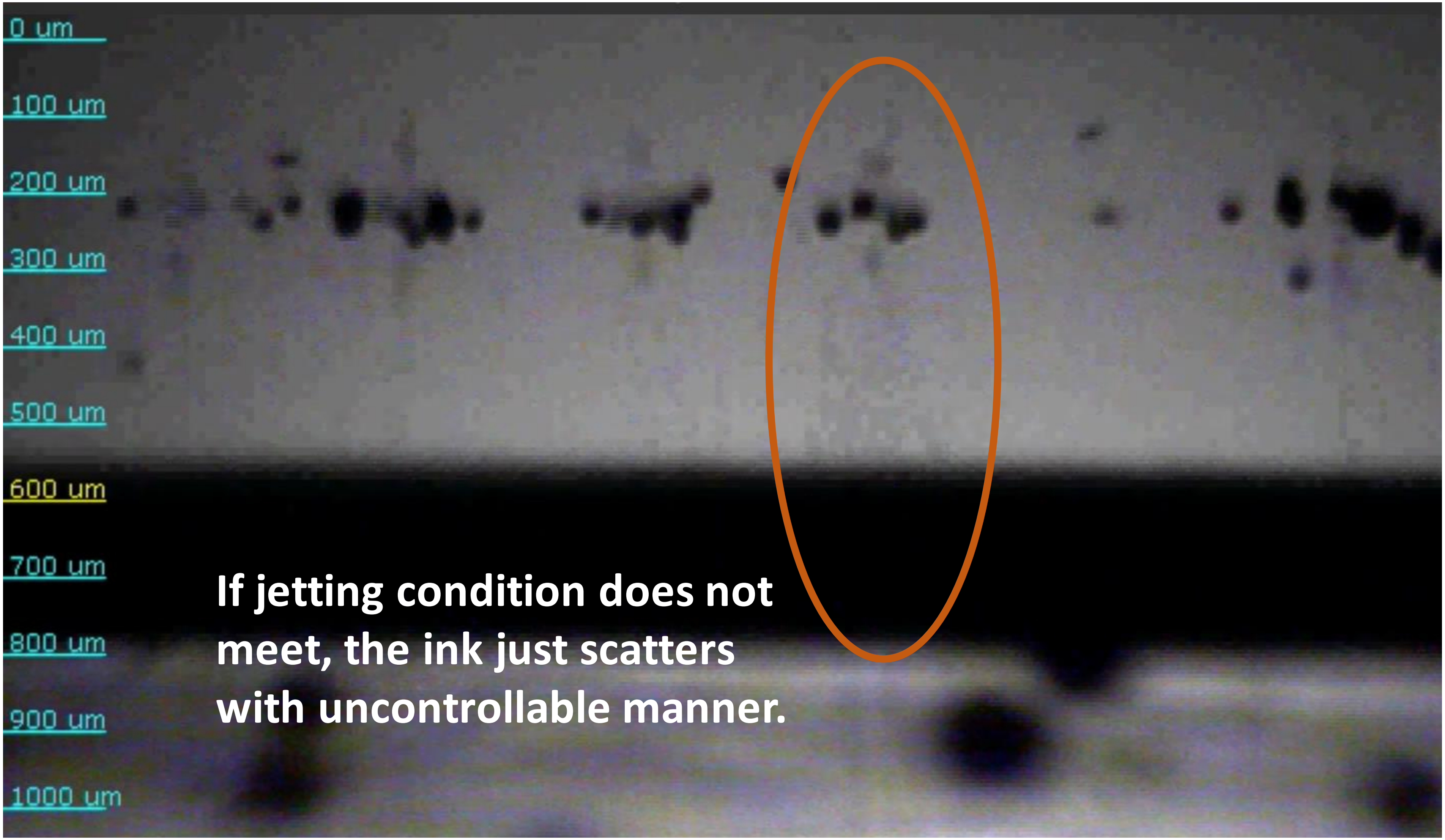
# Image processing to estimate particle size distribution



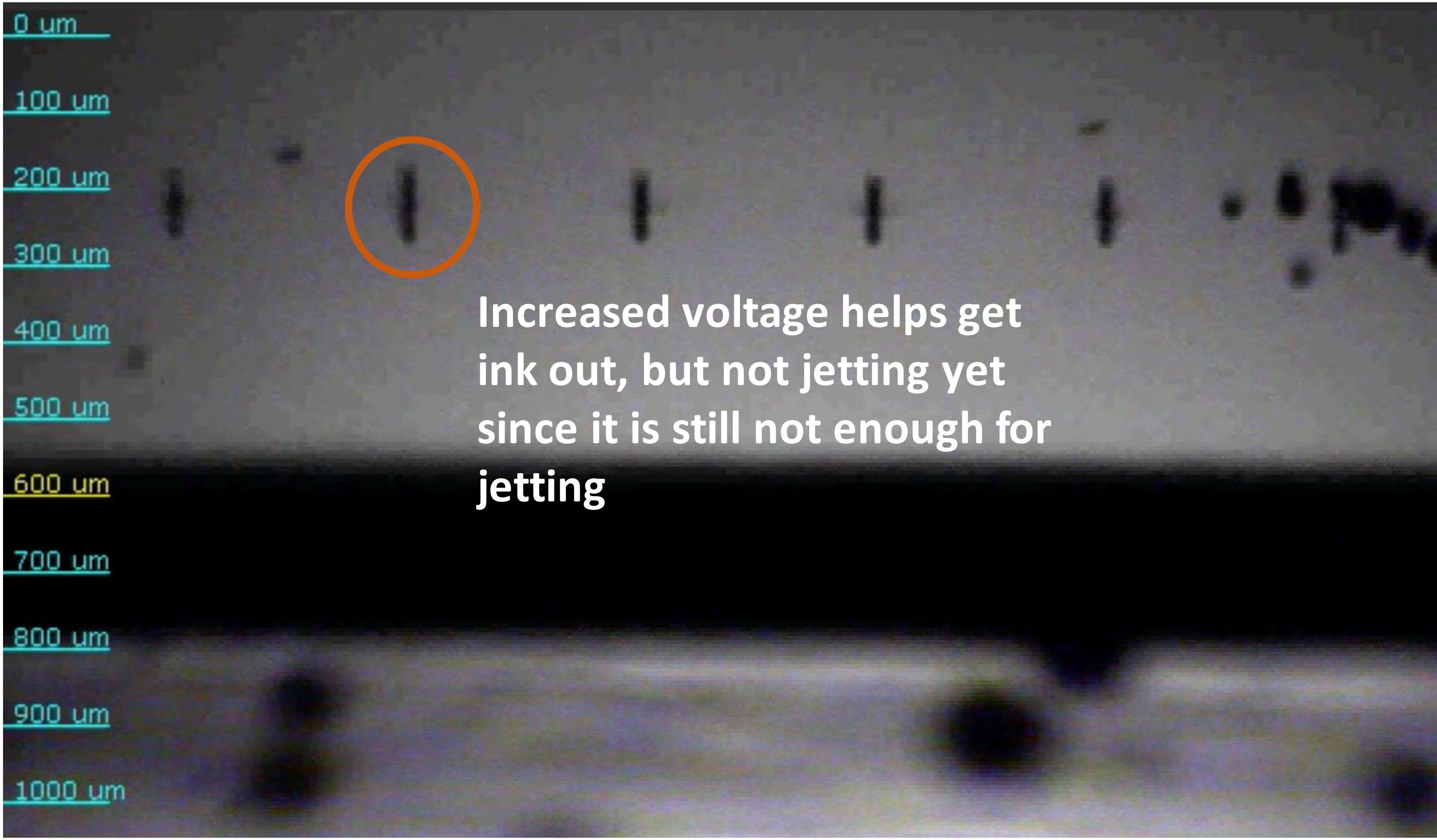

- SEM lets us determine particle size distribution and estimate particle density
- Wrote an image processing tool to estimate particle size distribution from SEM
- Source code will be provided

# Printing Test

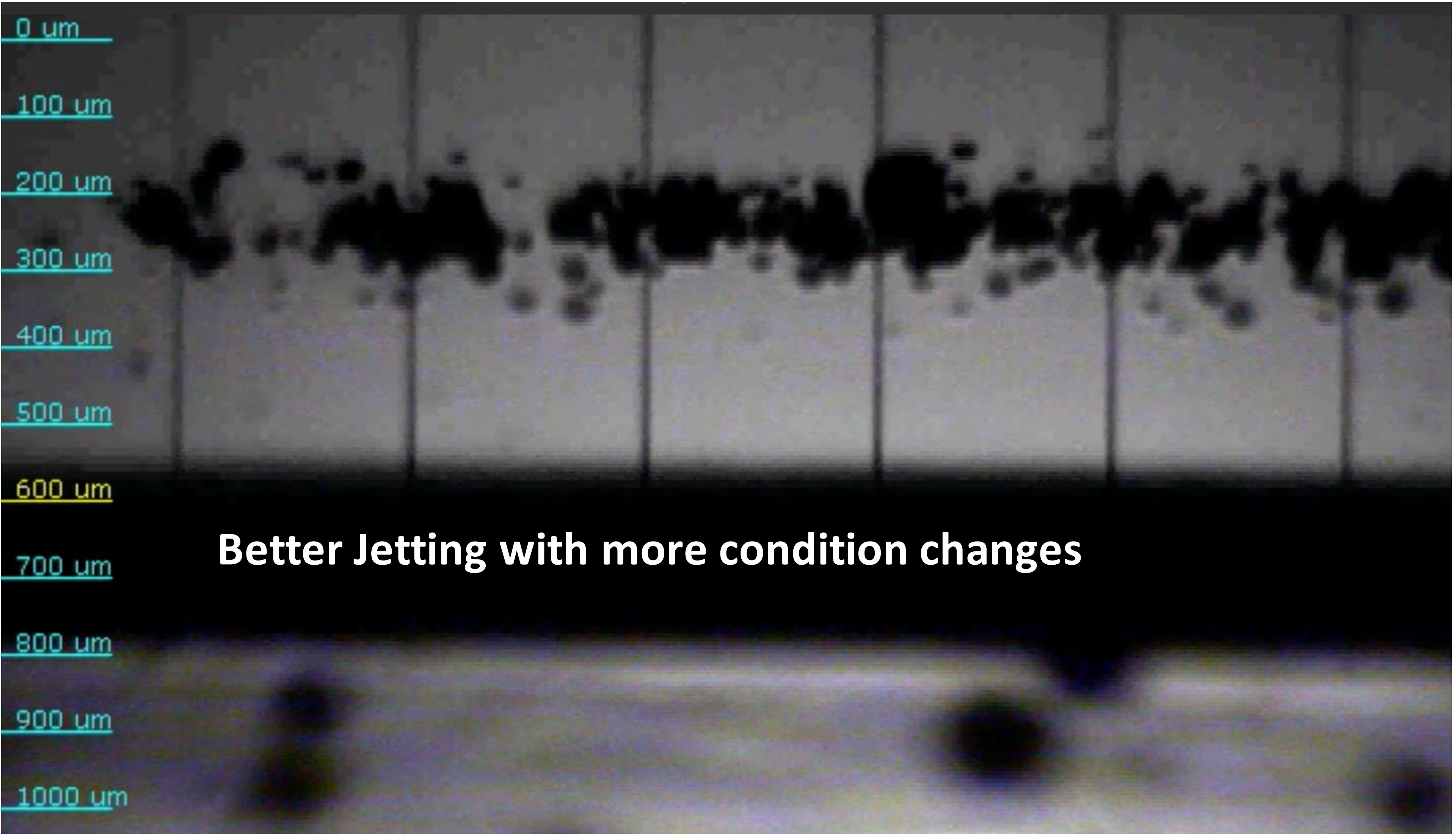



**If jetting condition does not meet, the ink just scatters with uncontrollable manner.**

# Printing Test



# Printing Test

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## Printing Test