

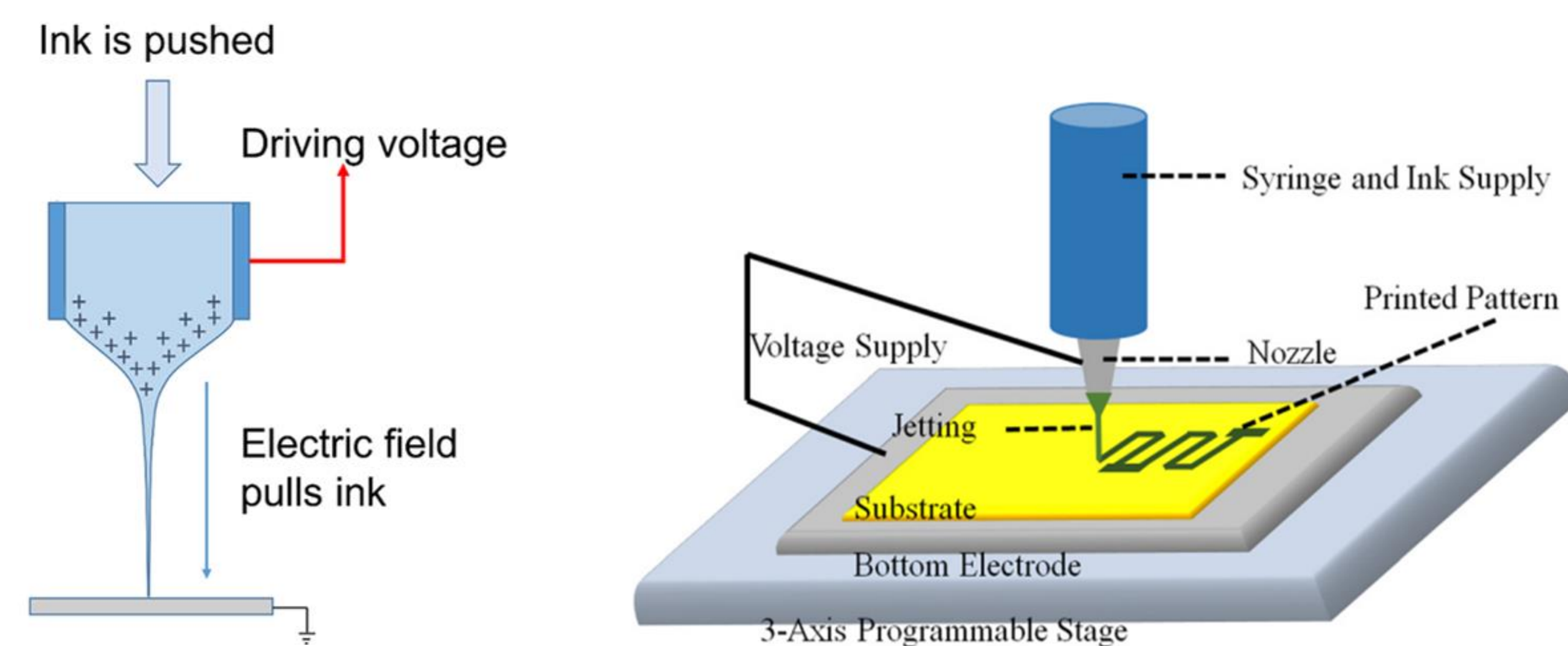
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### Stabilization of BaTiO<sub>3</sub> Nanoink with Surfactant and pH Control

#### Background

- The goal of this research is to produce a system for printing electronics out of colloiddally stable inks in a zero-gravity environment.
- Electrohydrodynamic (EHD) printing is an additive manufacturing technique capable of producing micron scale to the sub-micron scale patterns.<sup>2</sup>
- Ink suitable for EHD printing requires a highly stable suspension of nanoparticles.
- Silver nanoinks are used to print conductive lines for electronic devices.
- BaTiO<sub>3</sub> is a dielectric material that can be used to make capacitors and sensors due to the shifting of its Ti<sup>4+</sup> ion in its perovskite structure.
- The scope of this honors project was to improve the stability of the BaTiO<sub>3</sub> nanoink using surfactants and pH control



(1) Phung, T. H.; Oh, S.; Kwon, K.-S. *J. Vis. Exp.* 2018, No. 137.  
(2) Qin, H.; Cai, Y.; Dong, J.; Lee, Y.-S. *J. Manuf. Sci. Eng.* 2017, 139 (3), 031011.

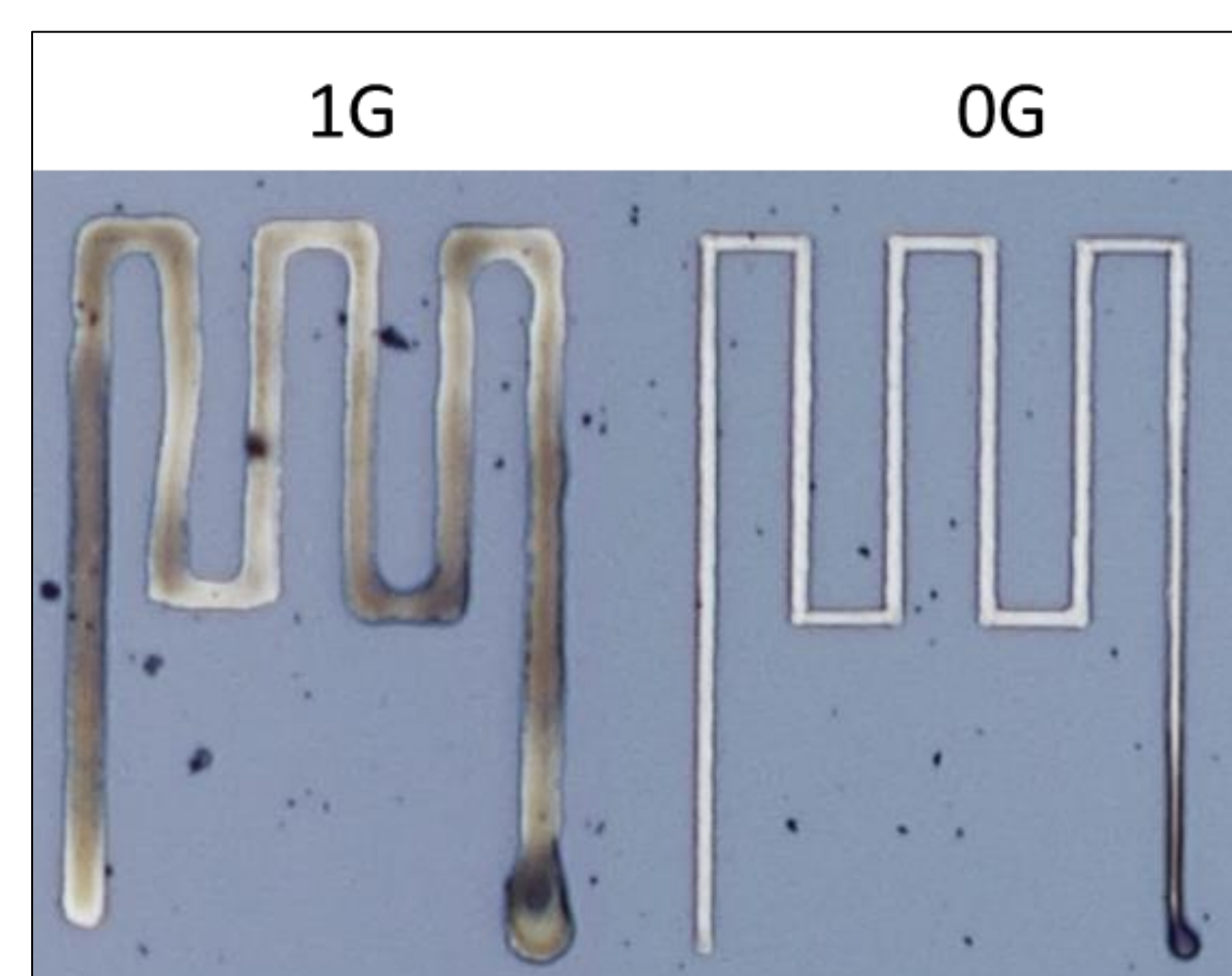
#### Zero-G Flight Test

Zero gravity printing is required for electronics to be produced in space. To evaluate this, a parabolic flight test was conducted to simulate a zero-g environment.

The flight test proved that EHD printing is still successful in zero gravity, however different settings are required than for printing in normal gravity.



Flight team with the EHD printer

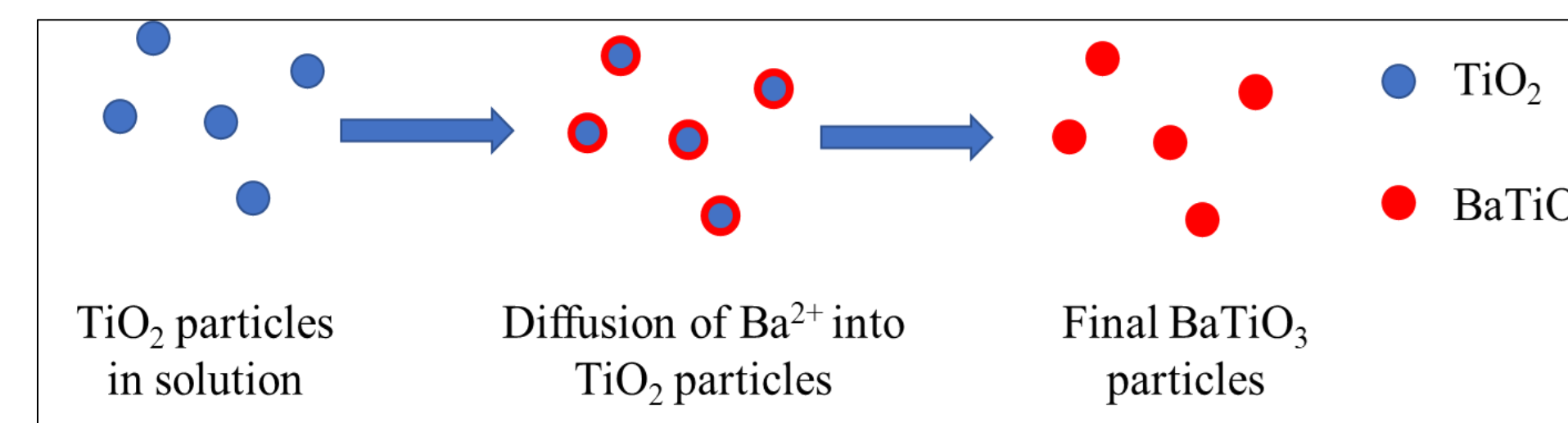


Silver patterns printed in normal gravity and zero-g with the same parameters

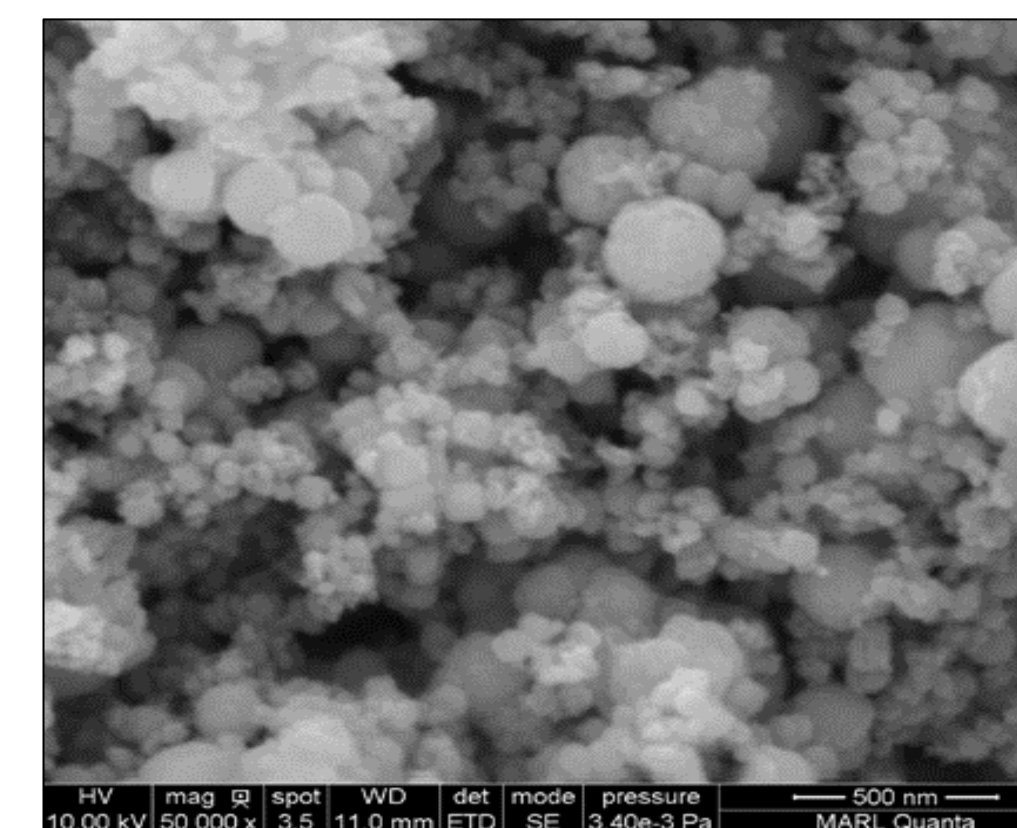


Printing experiment being conducted in zero-g.

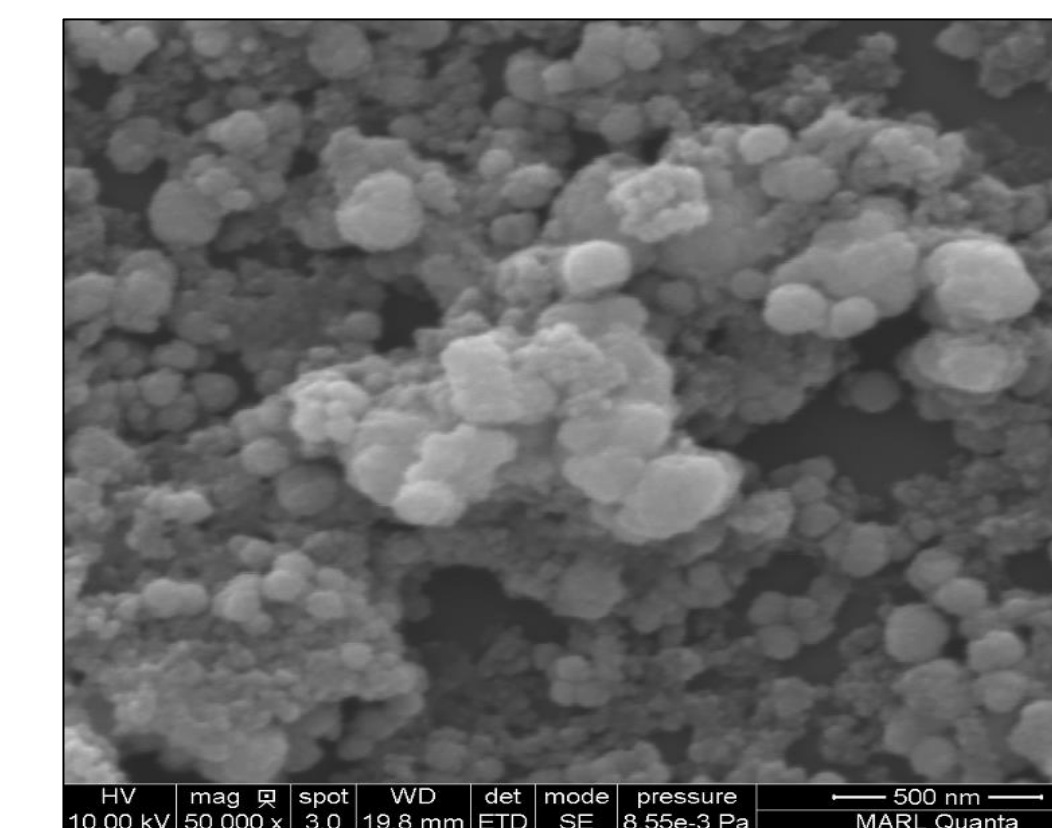
#### Synthesis



La-doped BaTiO<sub>3</sub> was synthesized in a reaction that used TiCl<sub>4</sub>, Ba(CH<sub>3</sub>COO)<sub>2</sub>, and La<sub>2</sub>O<sub>3</sub> as precursors. This reaction produces TiO<sub>2</sub> nanoparticles with Ba<sup>2+</sup> and La<sup>3+</sup> diffusing into the structure in an NaOH solution. 2-hydroxyethyl cellulose (HEC) is also present in the solution to act as a capping and dispersing agent to aid in the stability of the nanoparticle suspension. In addition to aiding in the suspension of nanoparticles, HEC also shows the ability to control particle size.



Synthesis Without HEC



Synthesis With HEC

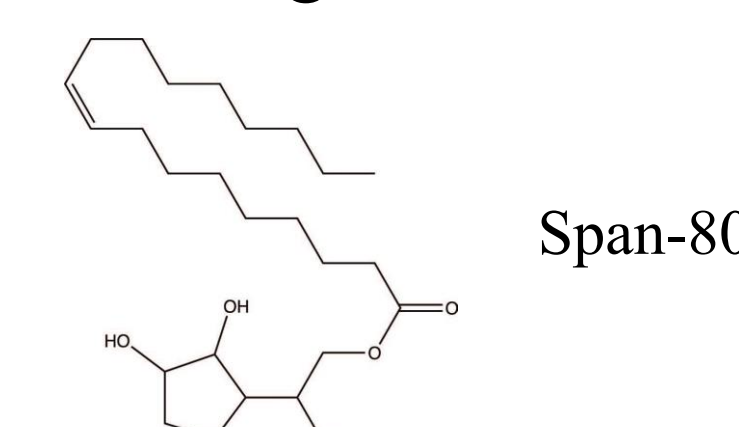
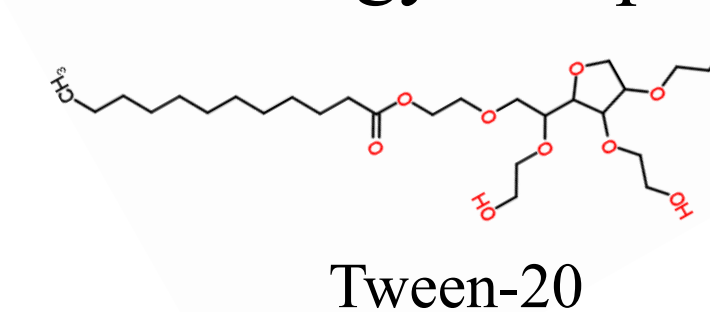
#### pH and Surfactant

Surfactant	Basic, pH 10	Neutral, pH 7	Acidic, pH 3
None (Control)	BC	NC	AC
Span-80	BS	NS	AS
Tween-20	BS	NT	AT

The tabulated treatments were applied to 9 samples of synthesized inks. Two surfactants were utilized: Tween-20 (polysorbate 20) and Span-80 (sorbitan monooleate). The inks were loaded to 40 wt% solids after synthesis and suspended in dimethyl sulfoxide (DMSO) with 2 wt% surfactant.

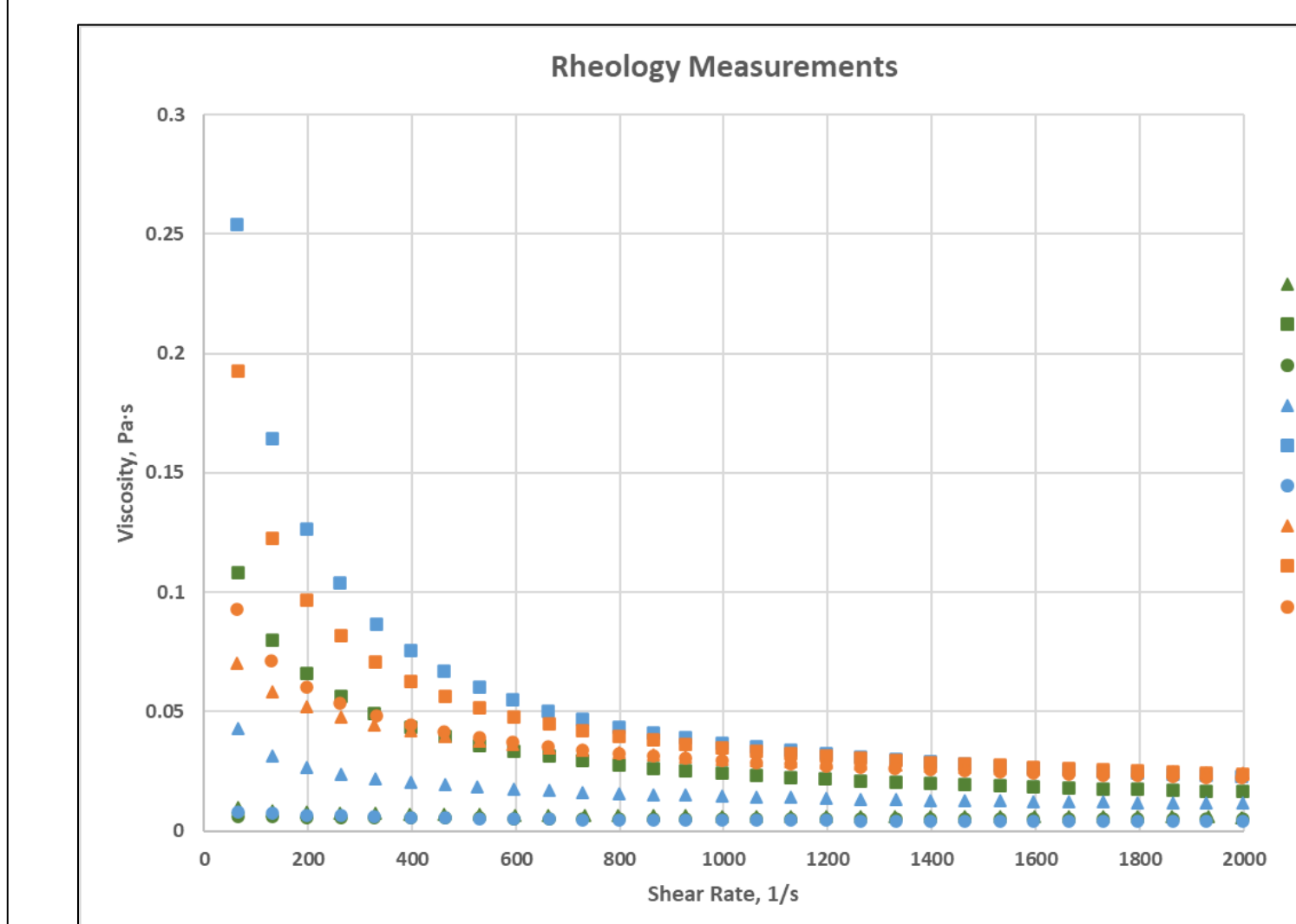
Component	wt%
BaTiO <sub>3</sub>	40
DMSO	58
Surfactant	2

pH was controlled with the addition of hydrochloric acid to the already-basic synthesized ink and validated using pH paper. The inks were vortex mixed and sonicated thoroughly to homogenize the surfactant and acid before rheology was performed.

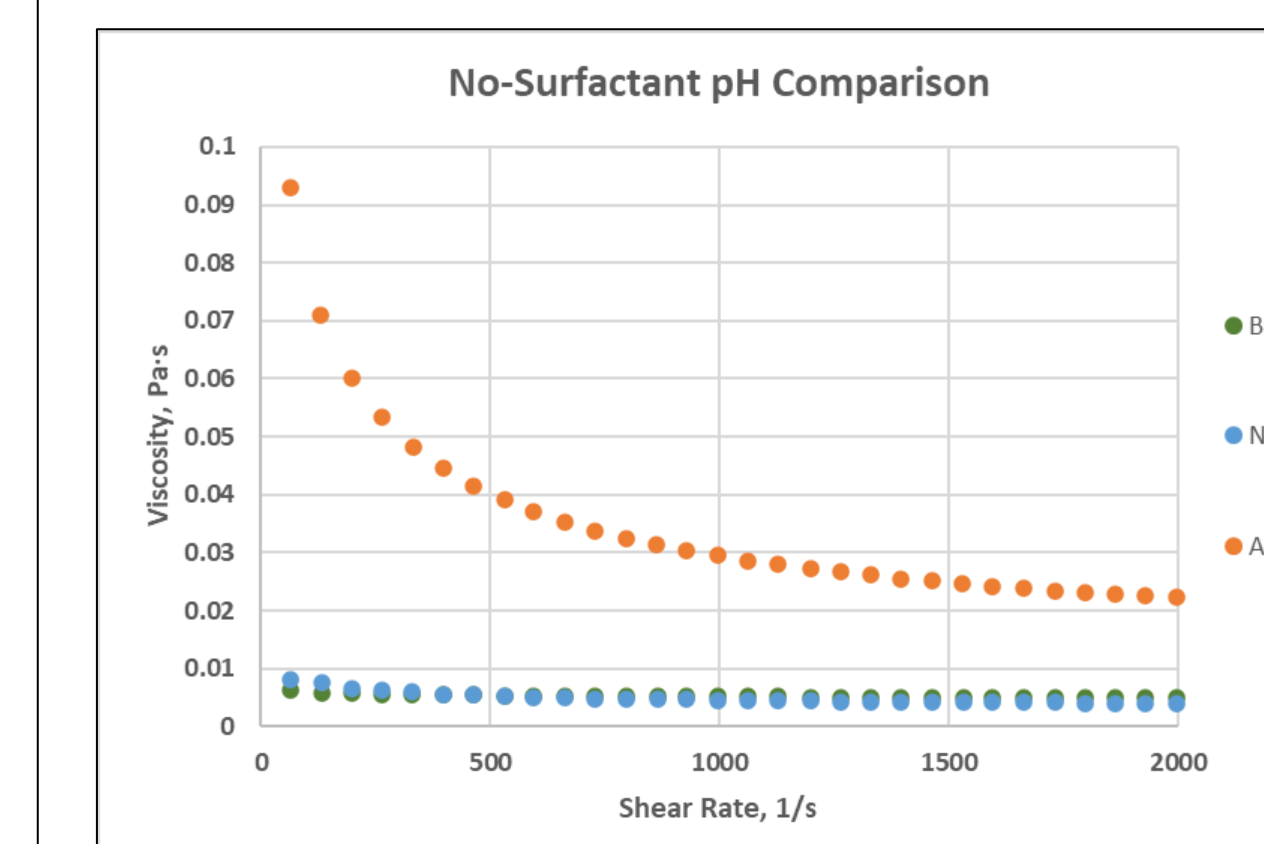


#### Results

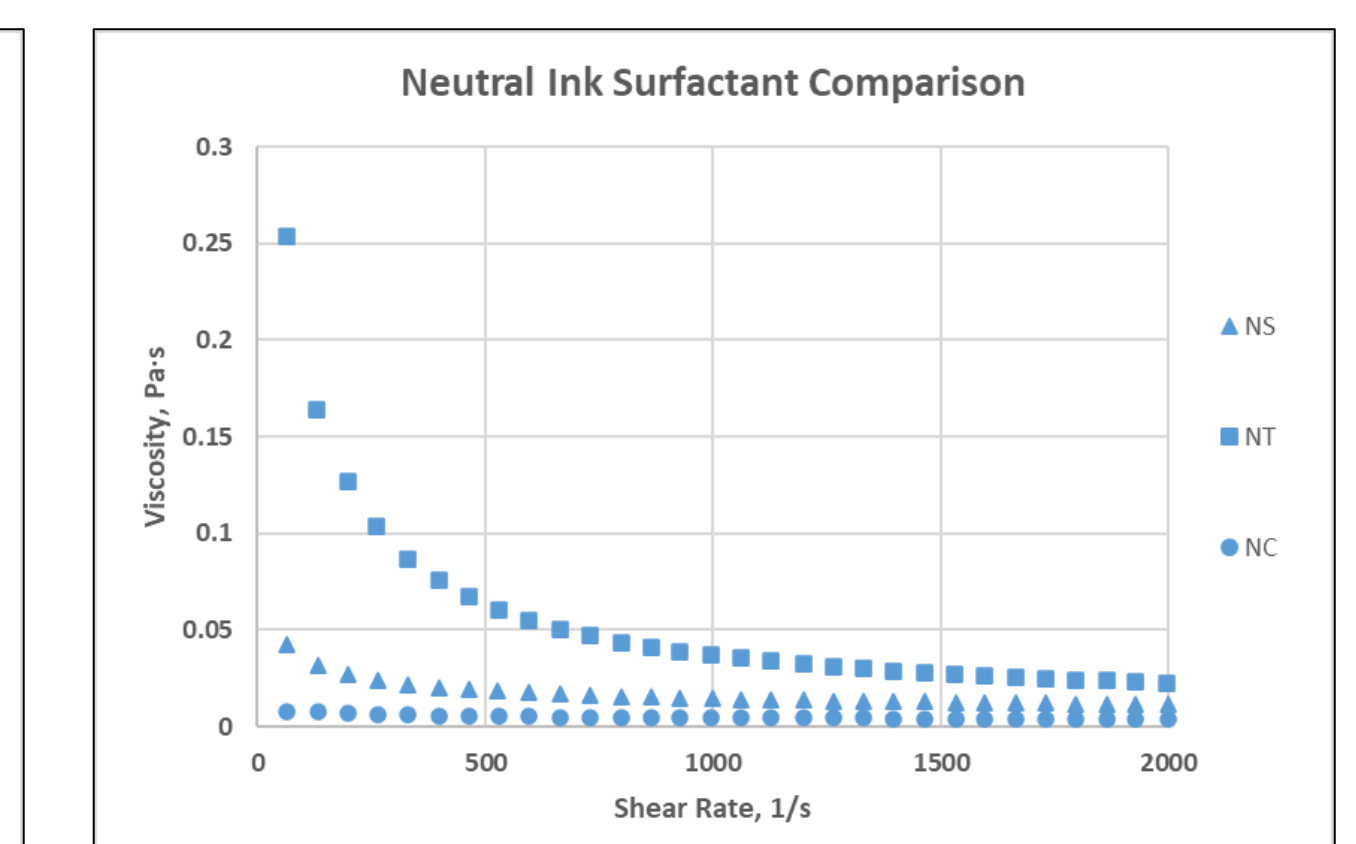
Rheology was performed to assess the stability of the produced inks. Increased viscosity and shear-thinning behavior indicates conglomeration, as clusters of particles are broken up during shearing and the ink becomes easier to shear.



Three of the inks found at the bottom of the graph showed excellent stability: BS, BC, and NC. The viscosity of these inks remained constant and showed minimal shear-thinning that was present in all other inks.



Acidity decreases stability

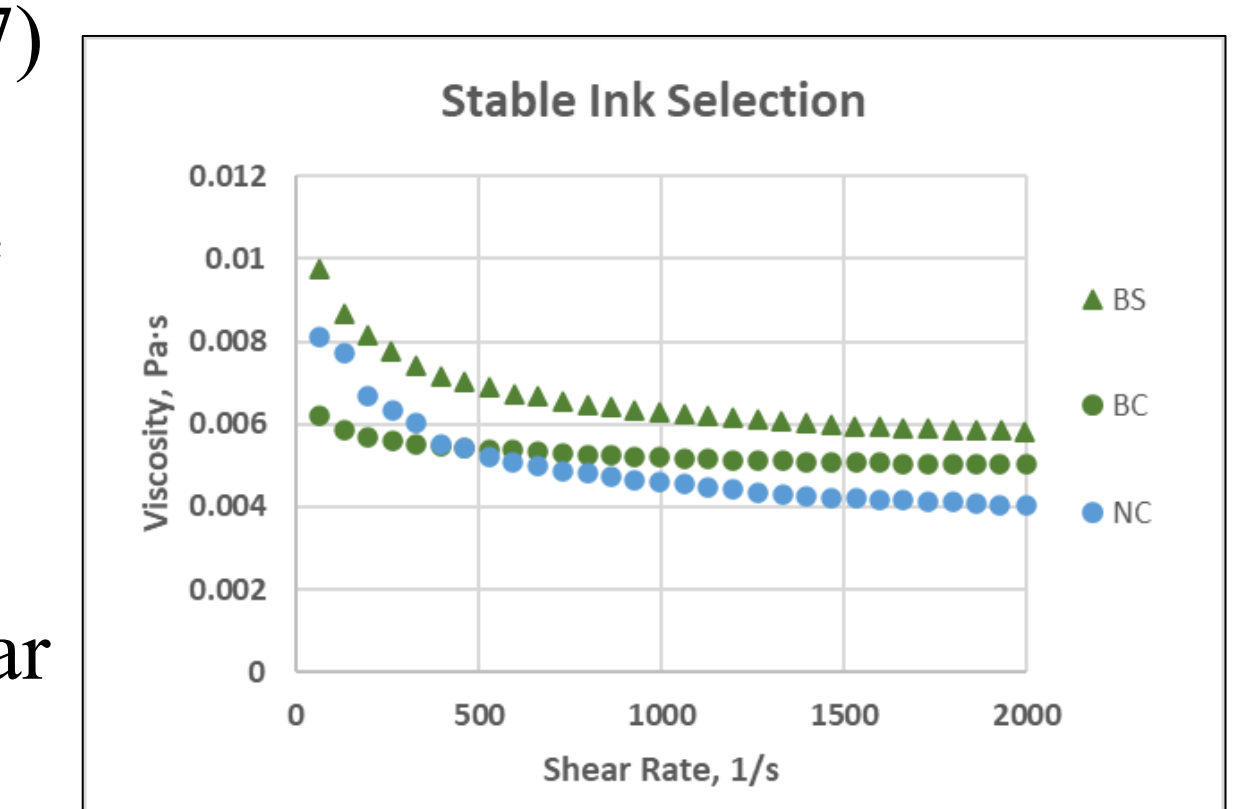


Tween-20 decreases stability

Analysis of the isolated control groups (neutral and surfactant-free inks, respectively) showed a clear negative effect of low pH and Tween 20 individually.

#### Conclusions

Basic (pH = 10) and neutral (pH = 7) inks were the most stable. Span-80 was found to have little effect while Tween-20 had a largely negative effect on stability. This could be explained by the structure of the surfactants, with the shorter nonpolar end of Tween-20 failing to adsorb onto the nanoparticle surface, serving only to increase viscosity.



Future work could explore additional surfactants, a finer range of pH values around 10, or inspect the surface of sintered circuits produced from these inks for a nanoparticle-scale comparison of surfactant effect.