Sprayable Antibacterial Film: a Nanosilver Composite

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Materials Science and Engineering

Senior Capstone Design

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2. Technical Approach
3. Design
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   - Solution design
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Motivation

- Nanoparticles and medicine
  - Tailorability
  - Particle distribution
  - High surface area
- Nanoparticle-Polymer composites
  - Release-killing and capture-killing mechanisms
  - Coatings and films

* - Wall Street Journal Study, 2012

Chitosan-Nanosilver Composite

Chitosan

- Simple polysaccharide
- Heavily researched for antibacterial properties
- Can synthesize nanosilver *in situ*
- Nanoparticle dispersion

Nanosilver

- Broad-spectrum antibacterial capabilities
- Tailor size and distribution
- Multiple simple synthesis methods

Design Goals

1. Film that adheres to Al_2O_3 – the iPhone surface
2. Maximum 50μm thickness
3. Spray application
4. Overnight drying
5. Maximum colony forming units of $5x10^5$/ml

Technical Approach - Solution

- Chitosan solubility
  - Soluble in acetic acid
  - Easy to dissolve – no heat and minimal stirring
- Viscosity increases with added chitosan
  - Needs to be experimentally determined
  - Sprayable liquid – viscosity max. 200 cps (non-pressurized)
  - Assume nanoparticles are too small to affect viscosity
- Nanoparticle settling (Stoke's law)

$$V_0 = \frac{d^2(\rho_s - \rho)\,g}{18\mu}$$

Technical Approach - Nanoparticles

- Synthesis

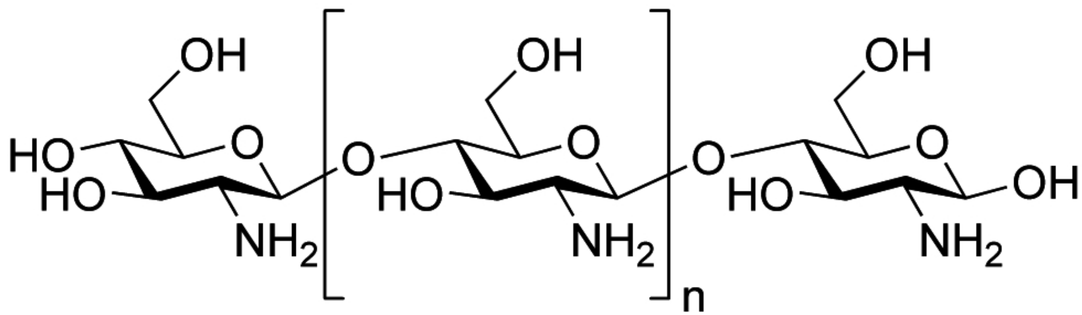
Step A: The adsorption of silver ions onto chitosan.

$$\text{R-NH}_2 + \text{H}^+ \rightleftharpoons \text{R-NH}_3^+$$
$$\text{R-NH}_2 + \text{Ag}^+ \rightarrow \text{R-NH}_2\text{Ag}^+$$
$$\text{R-NH}_3^+ + \text{Ag}^+ \rightarrow \text{R-NH}_2\text{Ag}^+ + \text{H}^+$$
$$\text{R-NH}_2\text{Ag}^+ + \text{H}_2\text{O} \rightarrow \text{AgOH} + \text{R-NH}_3^+$$

Step B: The formation of silver NPs–chitosan bioconjugates.

$$2\text{AgOH} \rightleftharpoons 2\text{Ag}^+ + 2\text{OH}^- \rightleftharpoons \text{Ag}_2\text{O} + \text{H}_2\text{O}$$
$$\text{Ag}_2\text{O} + \text{R}'\text{CH}_2\text{OH} \rightarrow \text{R}'\text{CHO} + 2\text{Ag} + 2\text{H}_2\text{O}$$
$$\boxed{\text{Ag}_2\text{O} + \text{R}'\text{CHO} \rightarrow R'\text{COO}^- + 2\text{Ag} + 2\text{H}_2\text{O}}$$

- Chitosan allows for good dispersion due to complexing



Technical Approach - Nanoparticles

- Silver ions are the means for antibacterial activity
  - Greater concentrations of silver nitrate
  - Greater surface area allows for greater interaction

- Tradeoff: Gibbs-Thomson

$$r^* = \frac{2\gamma ln(C/C_0)}{k_b T}$$

- Changes in temperature also affect particle size

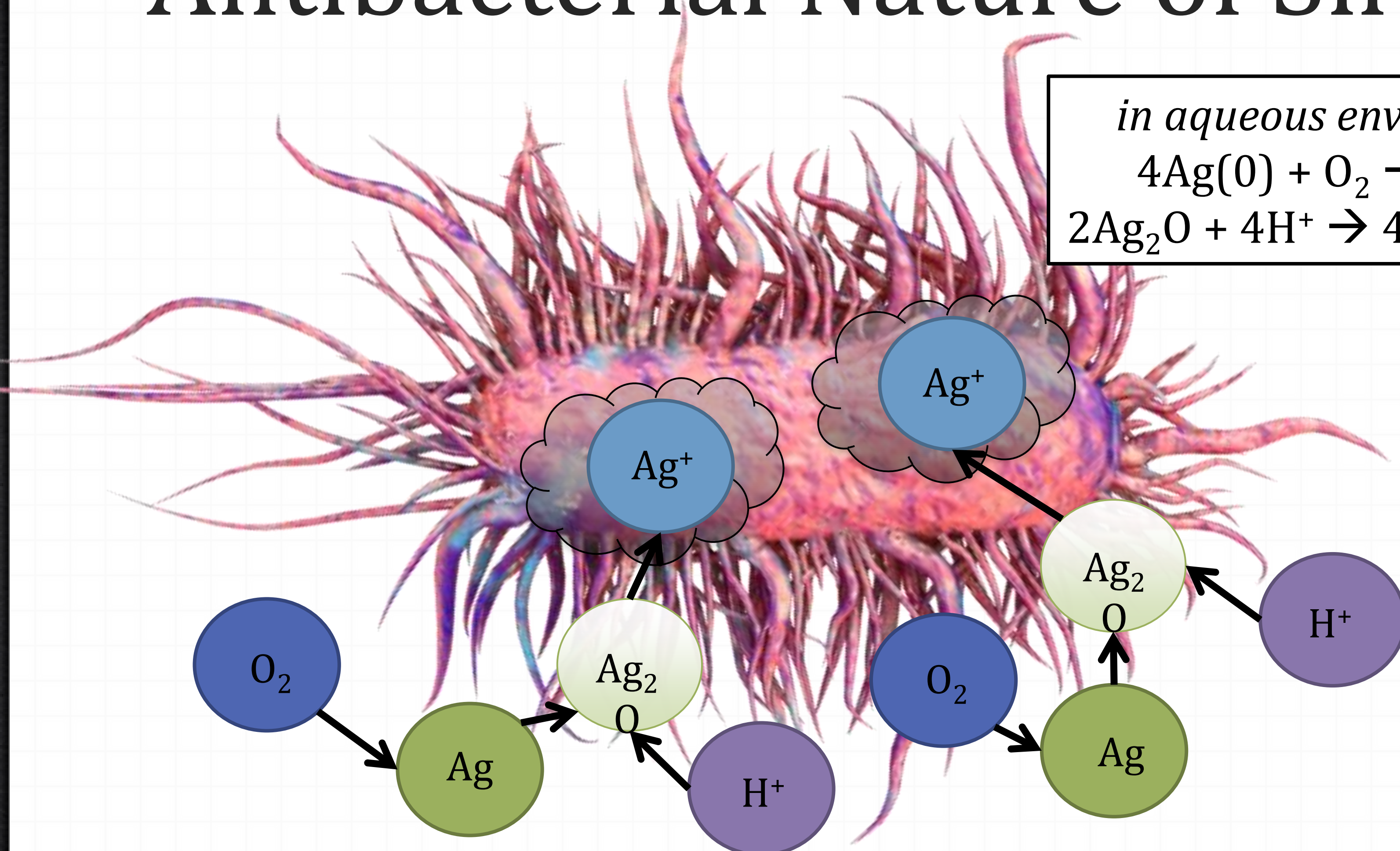
Experimentally analyze both temperature and concentration for particle size and antibacterial efficacy

Antibacterial Nature of Silver

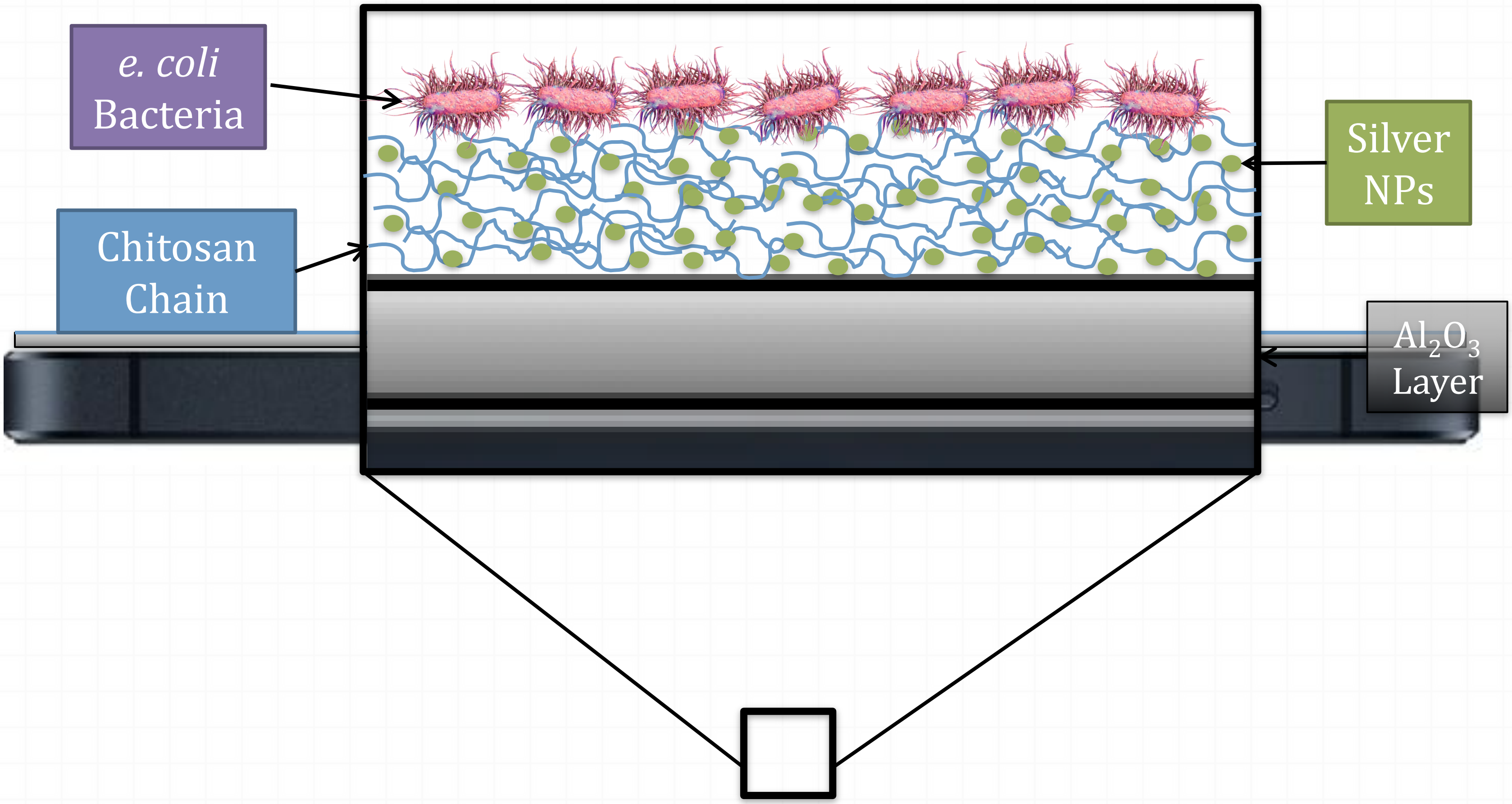
in aqueous environment

$4Ag(0) + O_2 \rightarrow 2Ag_2O$

$2Ag_2O + 4H^+ \rightarrow 4\mathbf{Ag^+} + 2H_2O$



Film Design

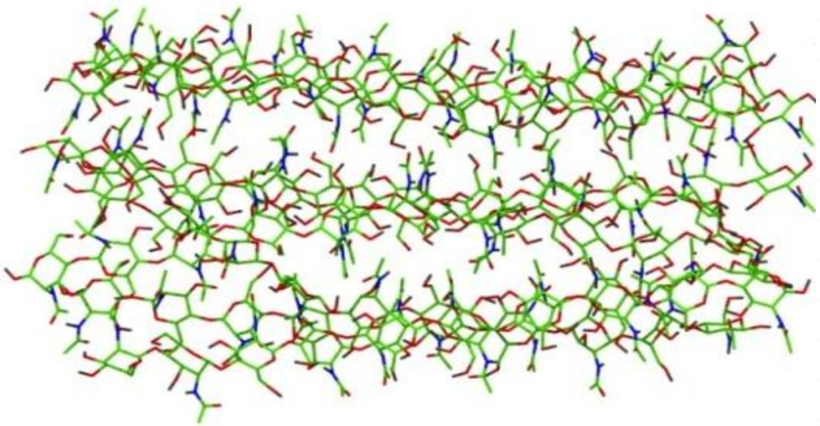


Critical Design Aspects

- Adhesion
  - Depends on the Al_2O_3 surface topography
  - Addition of levan to samples
- Antibacterial efficacy
  - Movement of silver ions
    - Aqueous solution
    - Hydration with PEG (polyethylene glycol)
    - Dispersion, near the surface of the film
  - Relation to nanoparticle size
    - Design for size control

Film Design

- Chitosan
  - Even arrangement, non-agglomerating



- Adhesion: van der Waals forces

$$A = \pi^2 C \varrho_1 \varrho_2$$

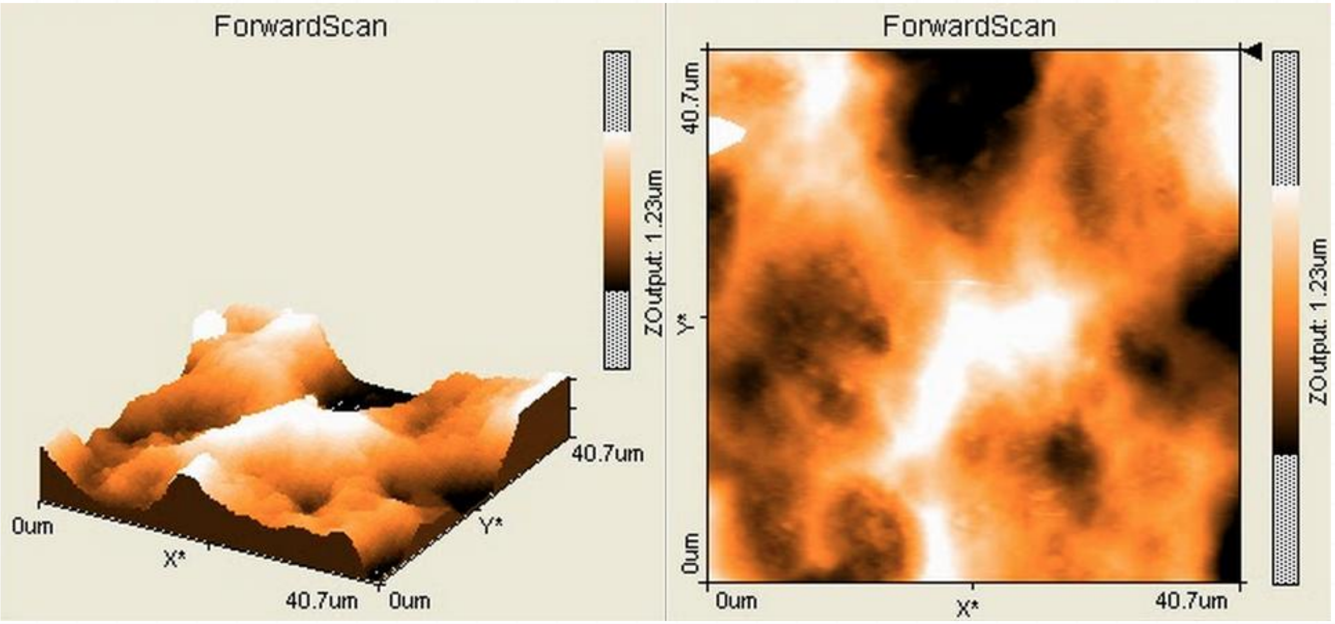
(~ 10^{-19} - 10^{-20} J)

$$W = \frac{A}{12\pi D^2}$$

$$F = \frac{A}{6\pi D^3}$$

Film Design

- Adhesion:
  - Mechanical adhesion
  - AFM analysis of iPhone – increased surface roughness promotes mechanical adhesion



Solution Design

- Viscosity
  - Maximum sprayable viscosity: **200cp**
  - Settling during drying:
    - Design: 50μm, nanoparticles ~50nm
    - Wet thickness : 63μm
    - Maximum settling velocity: 13μm/8hr = 1.625μm/hr

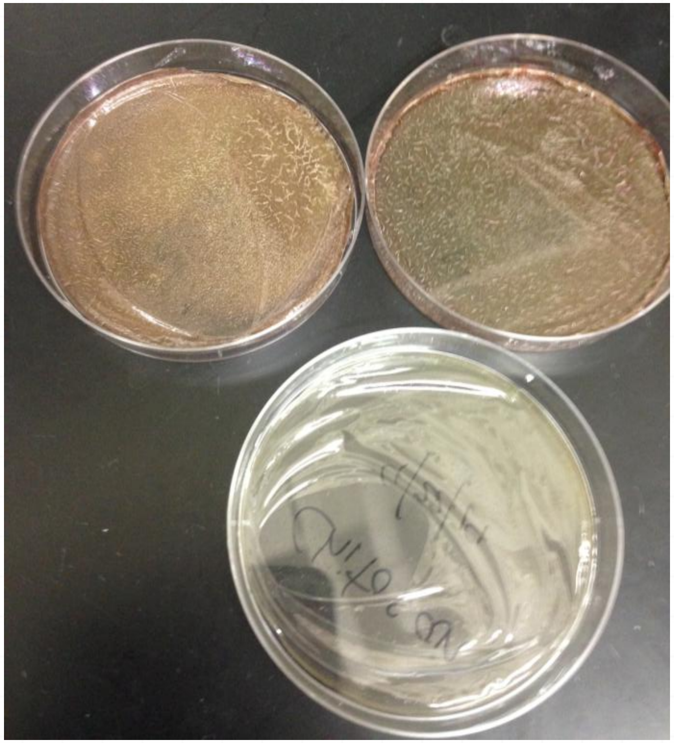
$$V_0 = \frac{d^2(\rho_s - \rho)\,g}{18\mu}$$

    - Ideal settling viscosity: **113cp**

$$\mu_{solution} = 0.8\mu_{spray} + 0.2\mu_{settle} = \boxed{\mathbf{182.6cp}}$$

Experimental Procedures

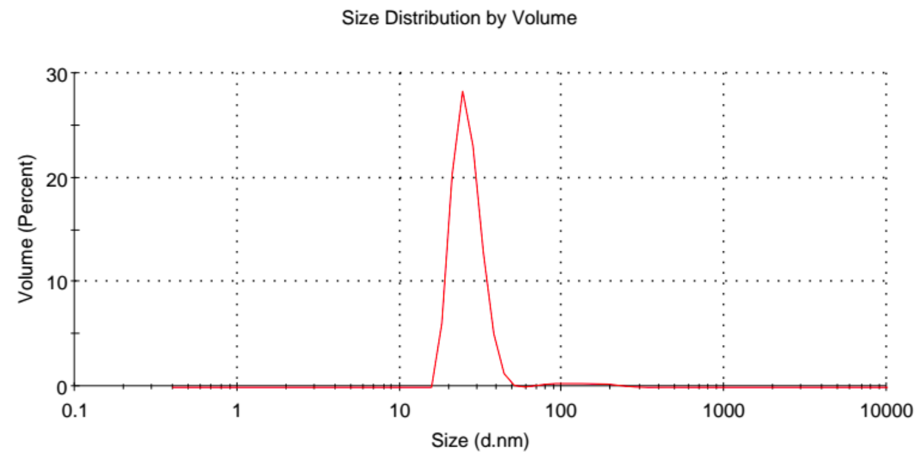
1. Synthesize nanoparticles (26mM and 52mM, 25°c – 95°c)

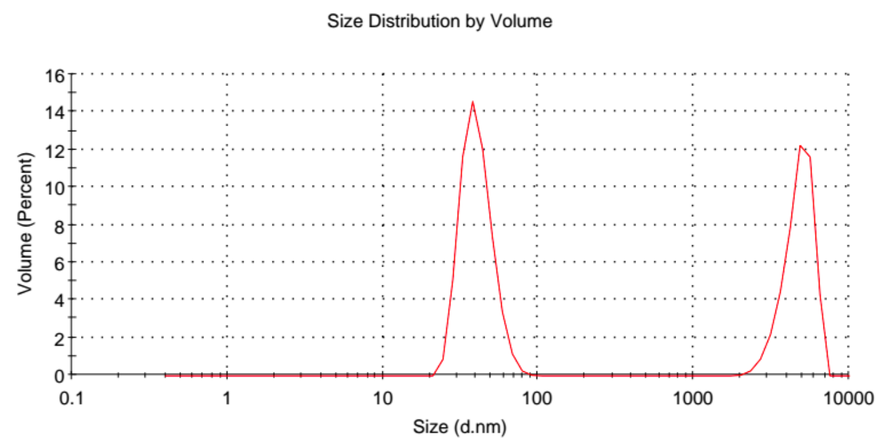


2. Make films

Solution Testing

Dynamic Light Scattering (ZetaSizer)





Solution Testing

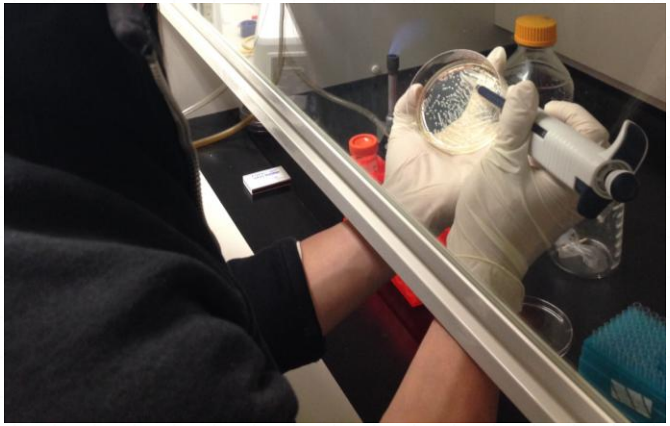
Viscometer

Viscosity measurements (centipoise)

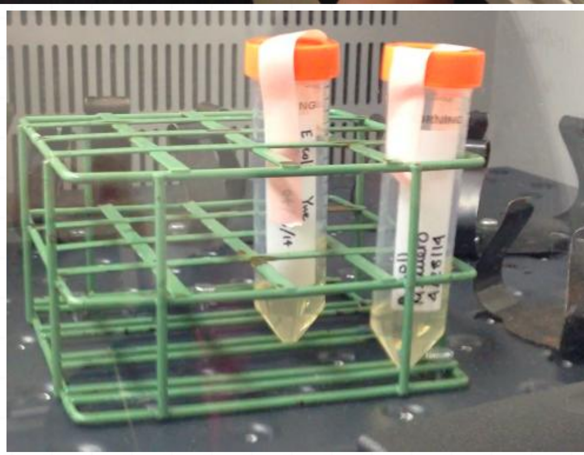
Synthesized with 10mg chitosan in 1% acetic acid

Sample	Run 1	Run 2	Run 3
26 mM #1	124.3	123.8	123.7
52 mM #1	120	119.1	119.6
26 mM #2	155.5	154	154.2
52 mM #2	158.8	161.2	159.2
26 mM #3	174.6	175	174.7
52 mM #3	158.5	158.2	157.7

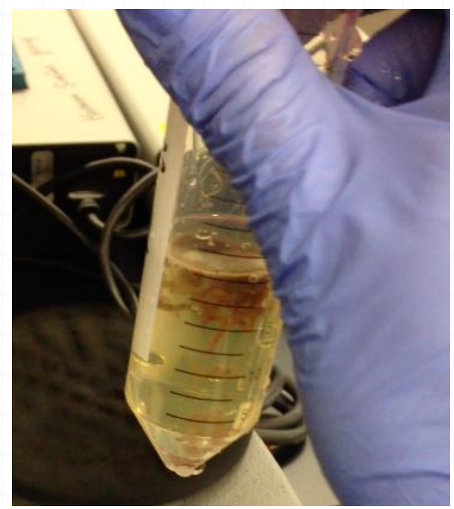
Experimental Procedure



4. Add bacterial agar to film (0h and 24h)

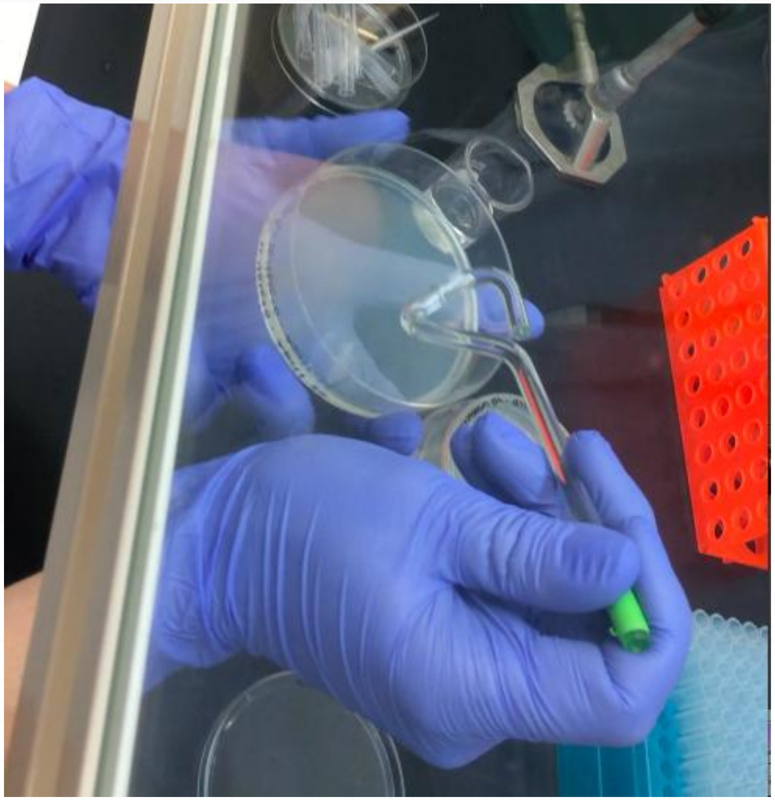


3. Grow bacteria solution

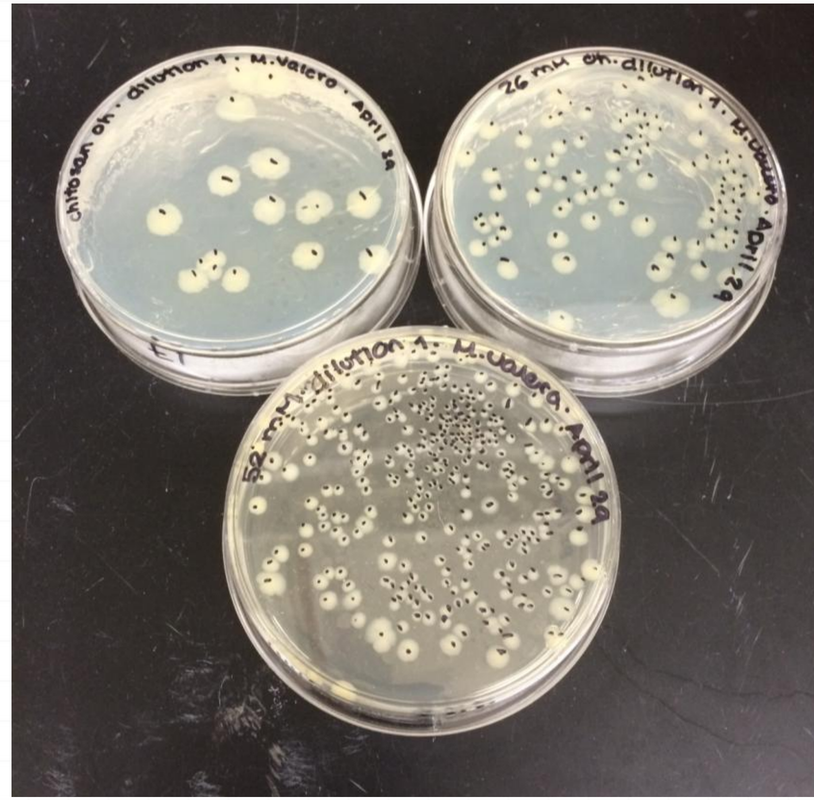


5. Place film in broth and grow bacteria from film

Experimental Procedure



6. Spread bacteria on agar film

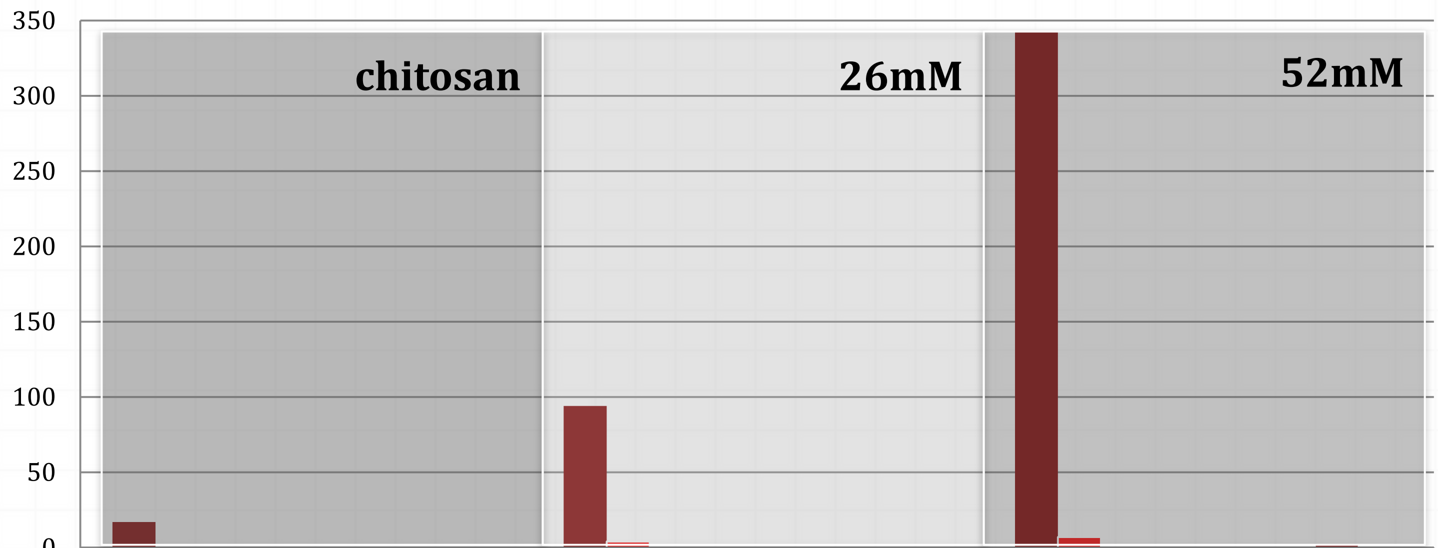


7. Grow and count bacteria cultures

Antibacterial Data

- Agar slurry: ~$3x10^6$ cells/ml
- Dilutions: (10μl of agar/600μl broth)
  - $4.9x10^4$ cells/ml, 806 cells/ml, 13 cells/ml

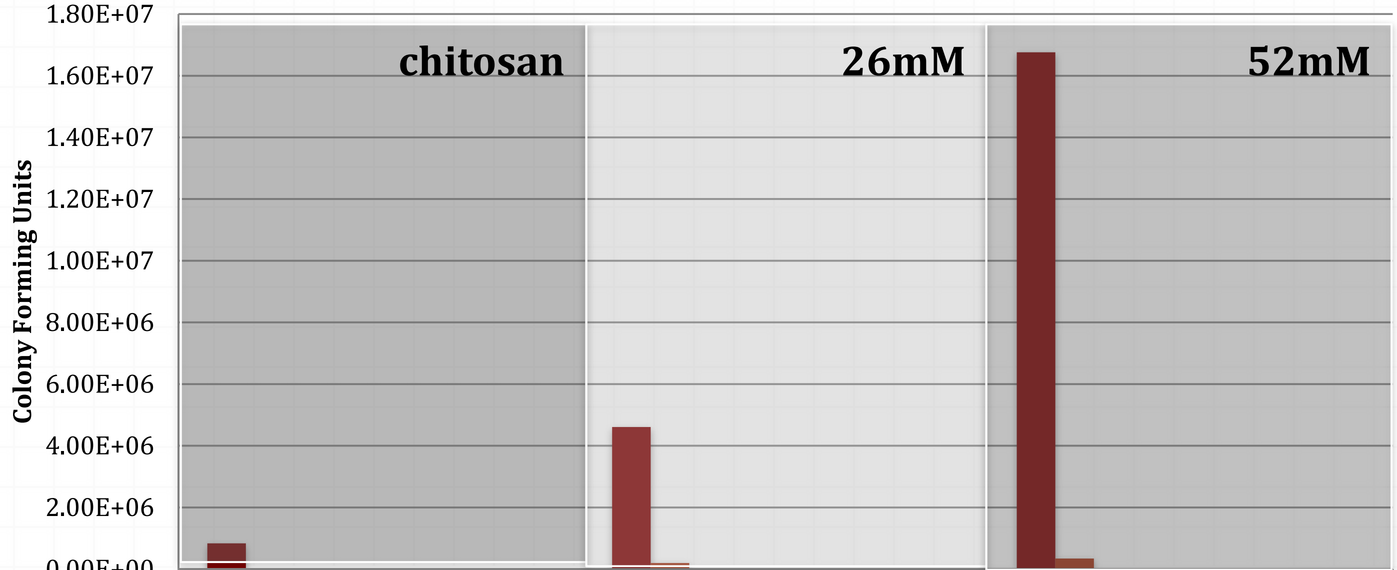
Colony Counts - 95°c synthesized nanoparticle film



	Dilution 1	Dilution 2	Dilution 3	Dilution 1	Dilution 2	Dilution 3	Dilution 1	Dilution 2	Dilution 3
0h	17	0	0	94	0	0	342	0	2
24h	0	0	0	4	0	0	7	0	1

Antibacterial Efficacy

CFU/ml



	Dilution 1	Dilution 2	Dilution 3	Dilution 1	Dilution 2	Dilution 3	Dilution 1	Dilution 2	Dilution 3
0h	8.33E+05	0.00E+00	0.00E+00	4.61E+06	0.00E+00	0.00E+00	1.68E+07	0.00E+00	2.60E+01
24h	0.00E+00	0.00E+00	0.00E+00	1.96E+05	0.00E+00	0.00E+00	3.43E+05	0.00E+00	1.30E+01

<u>Percent reduction:</u>

Chitosan – 100%

26mM – 95.7%

52mM – 97.9%

Experimental Obstacles

- UV sensitivity: some solution samples ruined before film development
- Film development depleted solution quantities for viscosity measurements
- Limitations with laboratory equipment and time
  - Limited amount of nanoparticle solution synthesized
  - Week-long antibacterial testing process
- Antibacterial testing is not always perfect
  - Some samples exhibited no bacterial cultures in the 0h control, indicating lack of initial bacteria in agar slurry

Prototyping

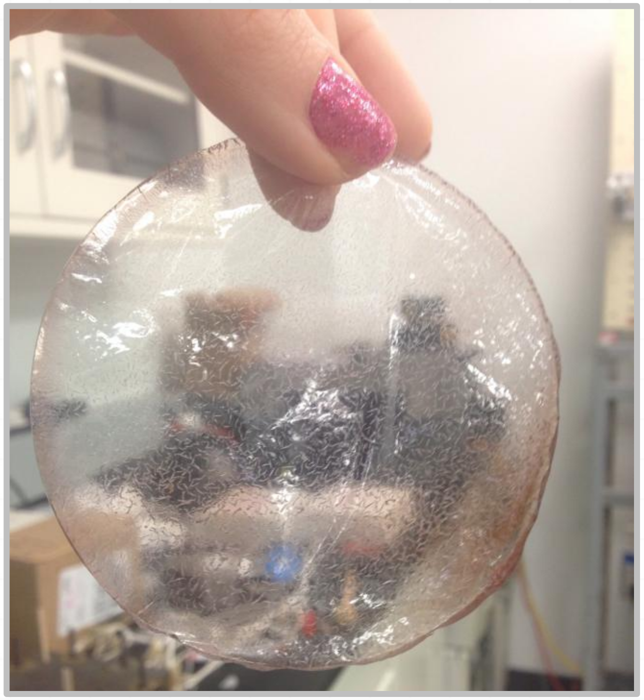
- Film that adheres to Al_2O_3 – the iPhone surface
- Maximum 50μm thickness
- Spray application
- Overnight drying
- Maximum colony forming units of $5x10^5$/ml

Prototyping

Adhesion

Adhered to aluminum foil

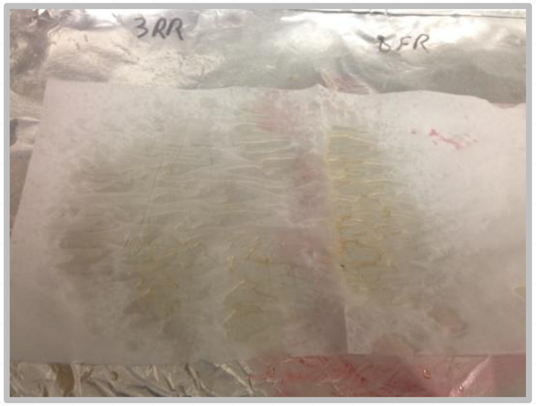
Thickness: avg. 66.5μm



Thin, but not as thin as design goal

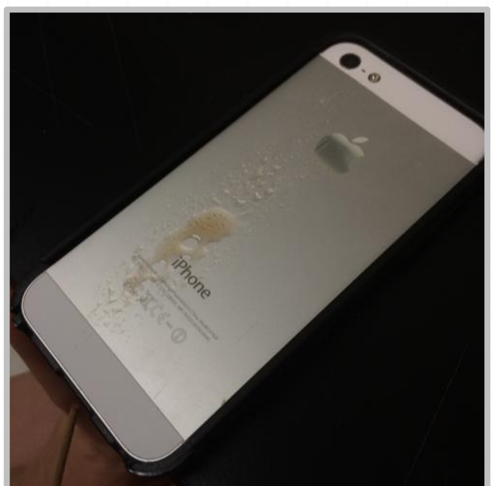
Prototyping

Spray Application

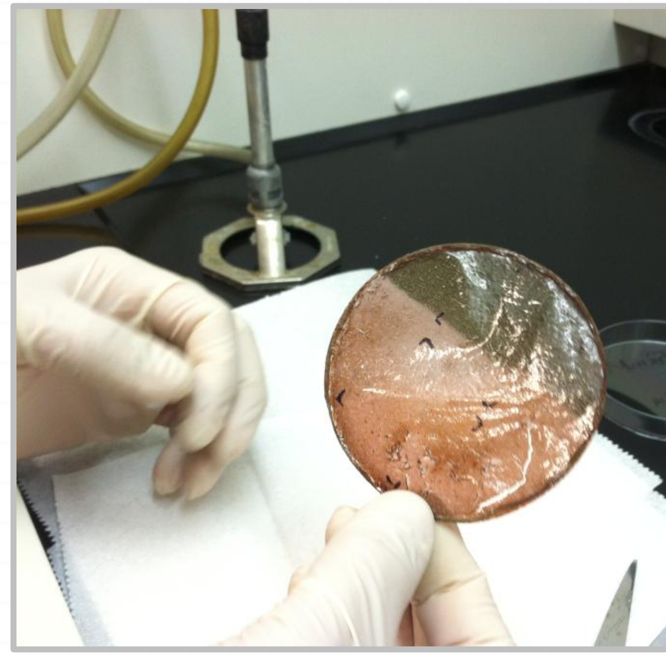


Good spray dispersion

Improper wetting: Al_2O_3 surface tension



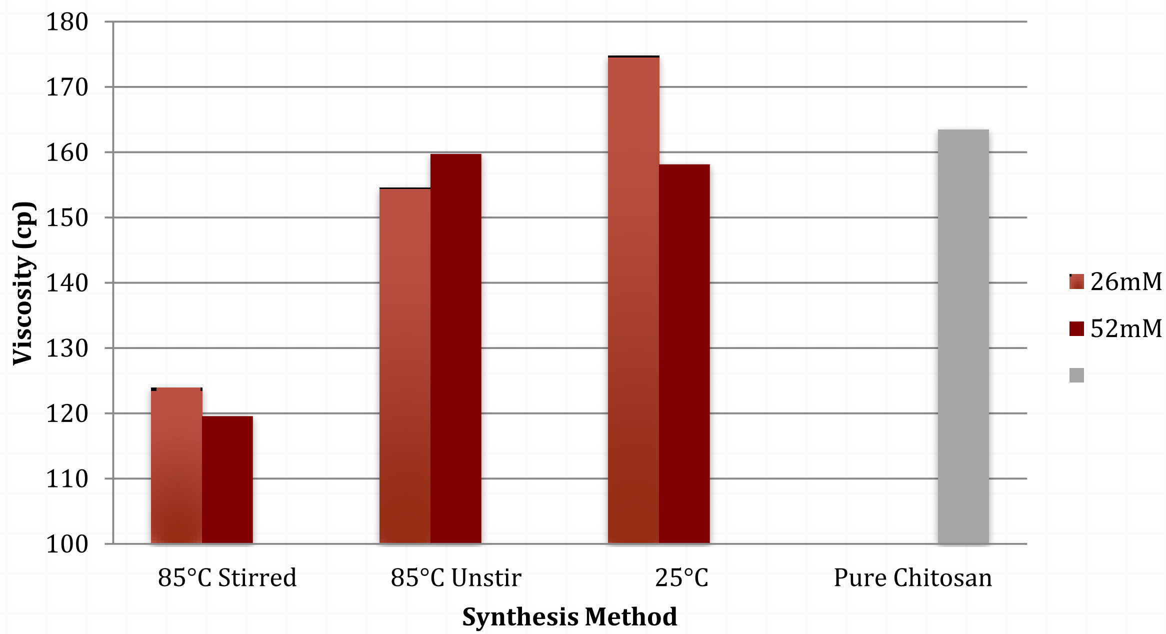
Overnight Drying



All films were made overnight and all showed proper drying

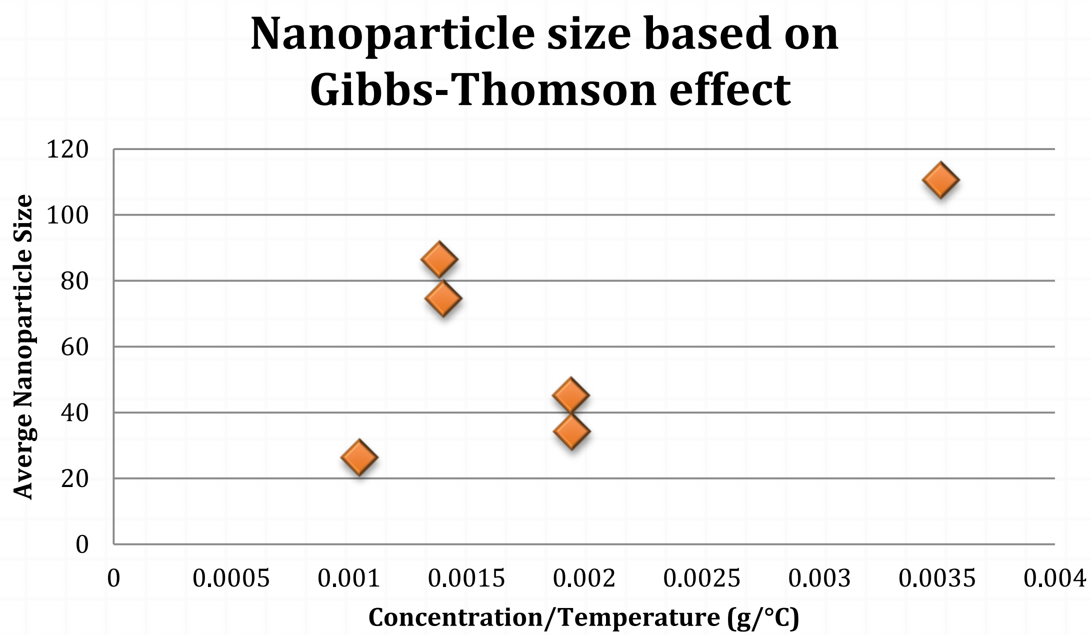
Design Conclusions

- 10mg chitosan in 1% acetic acid is a sprayable solution
  - Regardless of nanoparticle concentration
  - **Stirring of synthesis solution** decreases viscosity
    - Could add more chitosan to solutions for increased efficiency



Design Conclusions

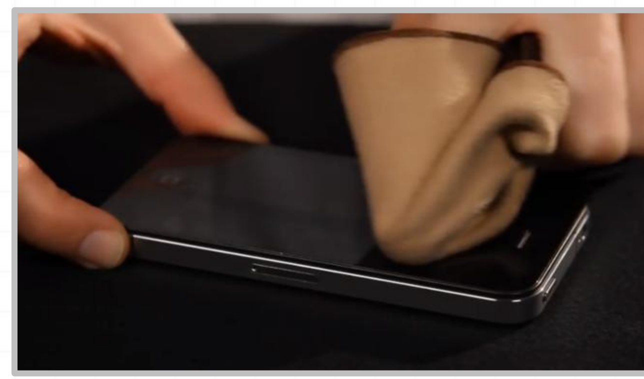
- Nanoparticle sizing
  - Shows some relation to Gibbs-Thomson
  - Not enough data to correlate to antibacterial properties



$$r^* = \frac{2\gamma ln(C/C_0)}{k_b T}$$

Design Conclusions

- Spray application
  - Surface energy of Al_2O_3 is too high – poor wetting
    - Design for another surface (commercial polymers have lower surface energies) → coating plastic cases
    - design another application method → aerosols or manual spreading via solution



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Project Summary

- Technical approach
  - Gibbs-Thomson effect
  - Solution viscosity
  - Nanoparticle size, distribution, ionization
- Experimental approach
  - Viscosity measurements
  - DLS measurements
  - Antibacterial efficacy
- Prototype
  - Accomplished film development and antibacterial properties
  - Film application method was not as designed

Thank You

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