Synthesis of Silver Nanoparticles via the Chemical Reduction Method

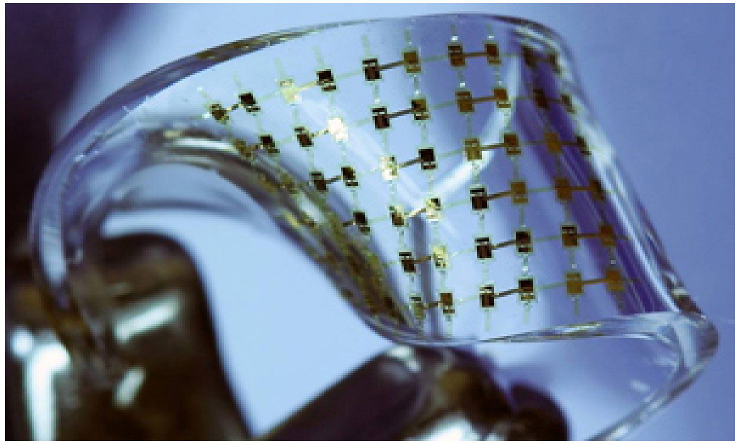
Caleb M. Wigham, Dr. Jeffrey J. Richards

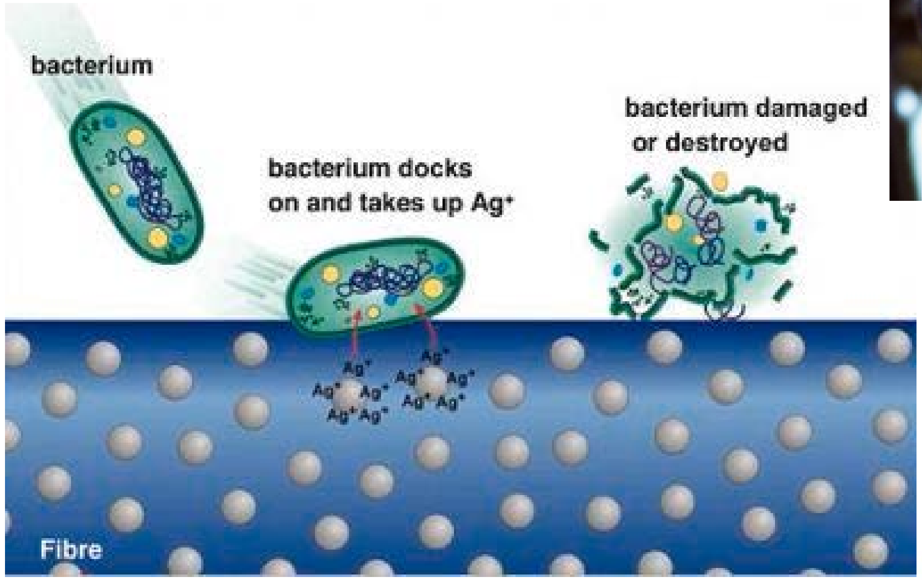
CHRNS CENTER FOR HIGH RESOLUTION NEUTRON SCATTERING NSF NIST

NIST Center for Neutron Research

Introduction

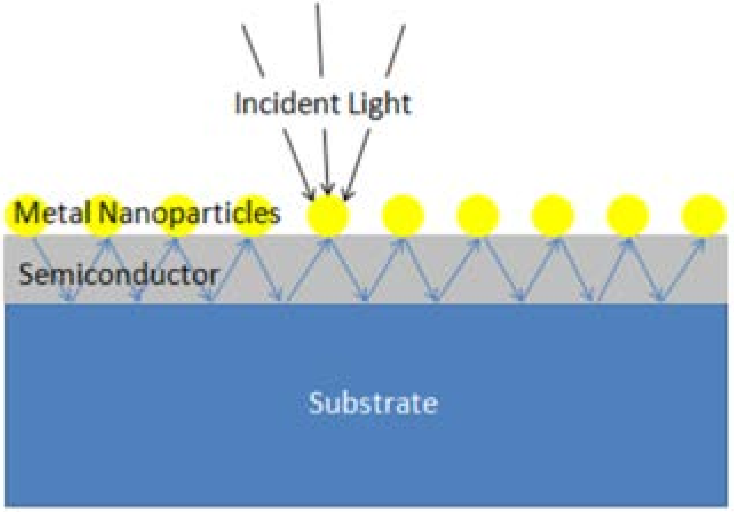
- Printable Conductive Coatings
  - *High electrical and thermal conductivity*





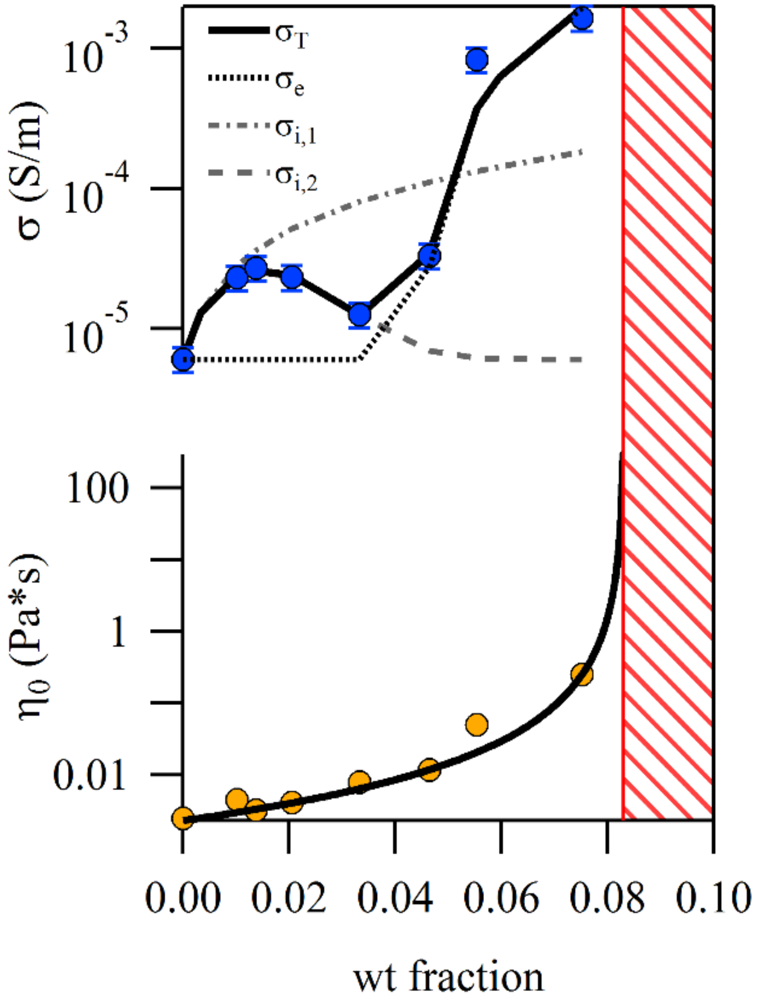
- Antimicrobial Coatings
  - *Bactericidal properties*

- Photovoltaics and Sensors
  - *Strong Interactions with Light*



https://www.medgadget.com/2009/01/flexible_electronics_might_signal_new_era_of_embeddable_medical_devices.html
https://stonybrook.digication.com/michael_santana/Final_Paper_Antimicrobial_Effects_of_Silver_Nanopa
https://en.wikipedia.org/wiki/Plasmonic_solar_cell#/media/File:PSC_using_Metal_Nanoparticles.png

Emerging Applications



Electrical Percolation

- Insulating particles with conductive surface layers have been shown to have excellent conductivity under the electrical percolation threshold
- Charges can be sent over distances *without direct physical contact* between particles
- Goal of this project is to study the behavior of conducting particles with insulating surface layers
- Controllable surface chemistry of conducting particles can lead to electrical storage applications such as flow batteries

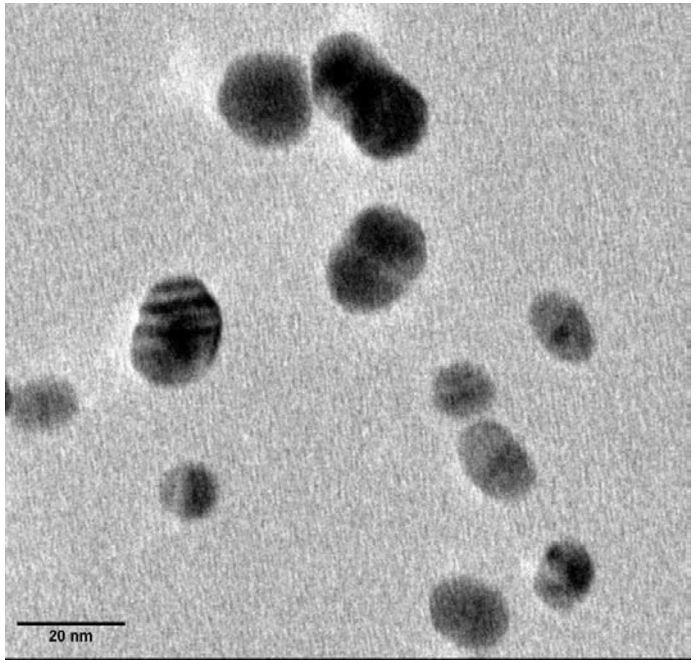
Richards, J. J.; Scherbarth, A. D.; Wagner, N. J.; Butler, P. D. *ACS Appl. Mater. Interfaces* **2016**, *8* (36), 24089–24096.

Project Goals

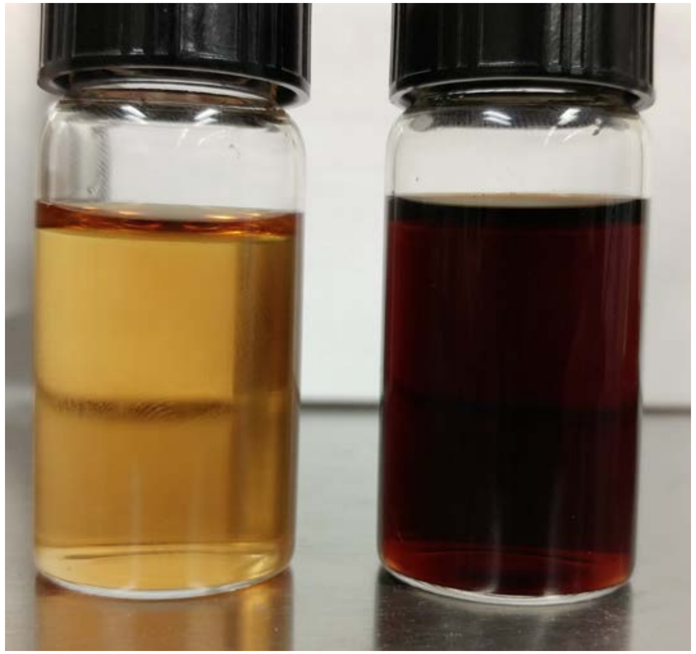
- Produce conductive particle solutions with insulating layers to promote colloidal stability
- Control surface chemistry and production of nanoparticles by exploring effects of varying reaction conditions and stabilizing methods
- Characterize physical properties by means of ultraviolet-visible spectroscopy (UV-VIS), transmission electron microscopy (TEM), and dynamic light scattering (DLS)

What are Silver Nanoparticles?

- Small silver particles on a length scale of 10 – 30 nm (4000x thinner than a human hair!)
- Typically spherical or elliptical in shape, though cubes and diamonds are possible
- When suspended, dilute particles appear yellow, turning reddish brown as concentration increases



TEM of silver nanospheres 10-20 nm in diameter

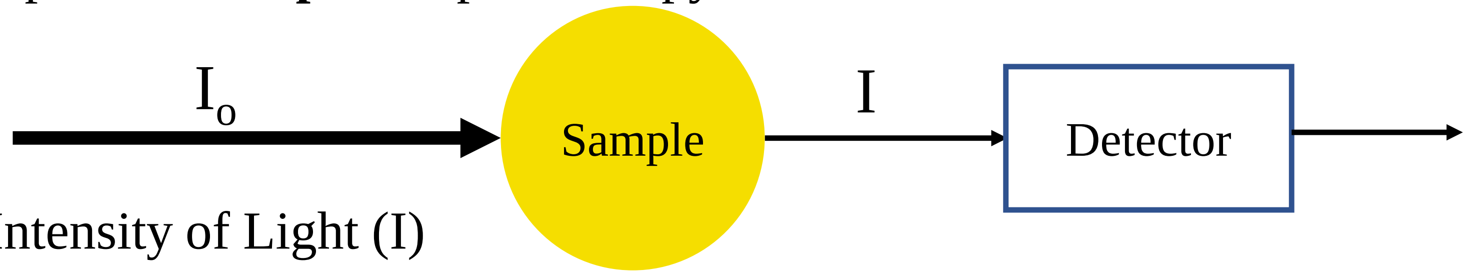


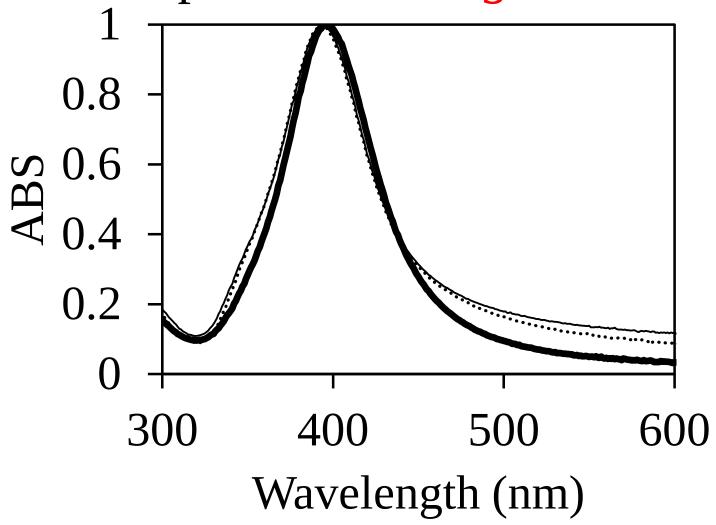
Stable Solutions of 1mM (left) and 5mM (right) silver nanoparticles

Surface Plasmon Resonance

Surface Plasmon Resonance: *Interaction* of free *electrons* confined in a metallic nanoparticle *with light*

- Optical **Absorption** Spectroscopy

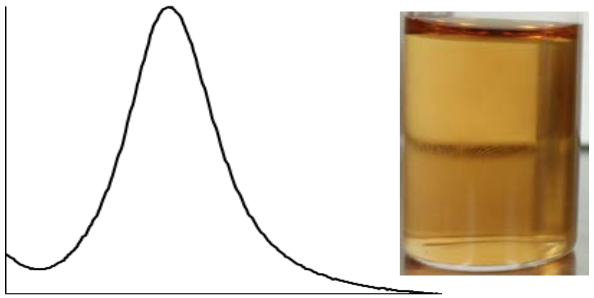




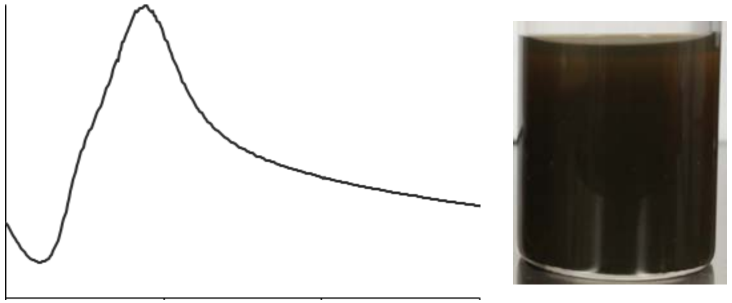
- Intensity of Light (I)
  Absorption = ln (I/I_o)

- Wavelength gives size *comparing* ability, not actual size

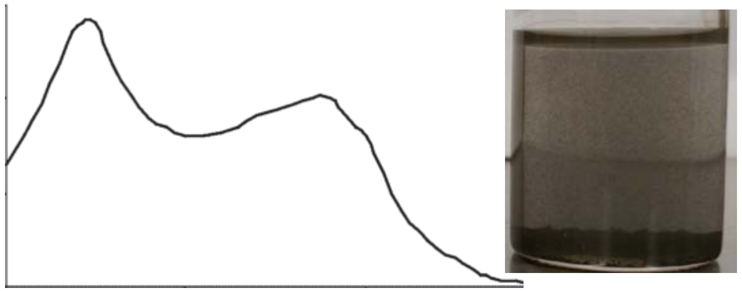
- Color indicates particle stability



Stable, Monodispersed



Stable, Shape Evolution (polydispersed)



Aggregated (Unstable)

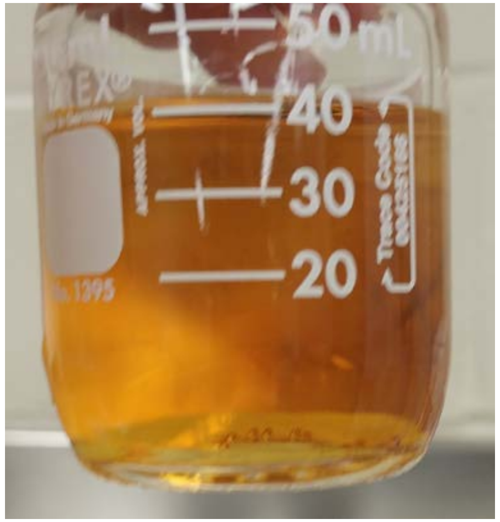
Mulfinger, L.; Solomon, S. D.; Bahadory, M.; Jeyarajasingam, A. V.; Rutkowsky, S. A.; Boritz, C. *J. Chem. Educ.* **2007**, *84* (2), 322.

Reduction of Silver Nitrate by Sodium Borohydride

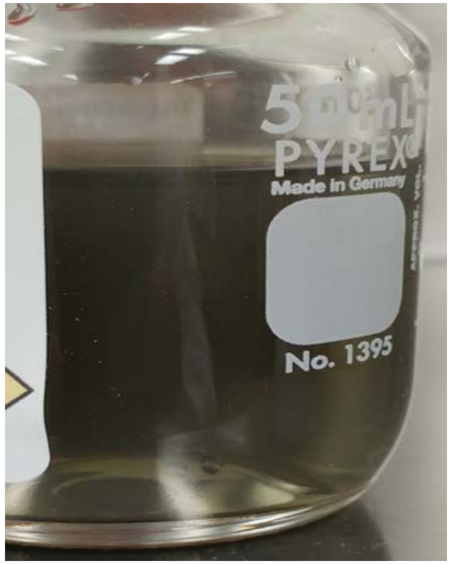
$$AgNO_3 + NaBH_{4(excess)} + 4H_2O_{(excess)} \rightarrow Ag_m + NaNO_3 + B(OH)_3 + 4H_2 + NaOH$$

- 2mM $NaBH_4$ prepared in ice-bath
- 1mM $AgNO_3$ added dropwise
- Addition time of 3 minutes

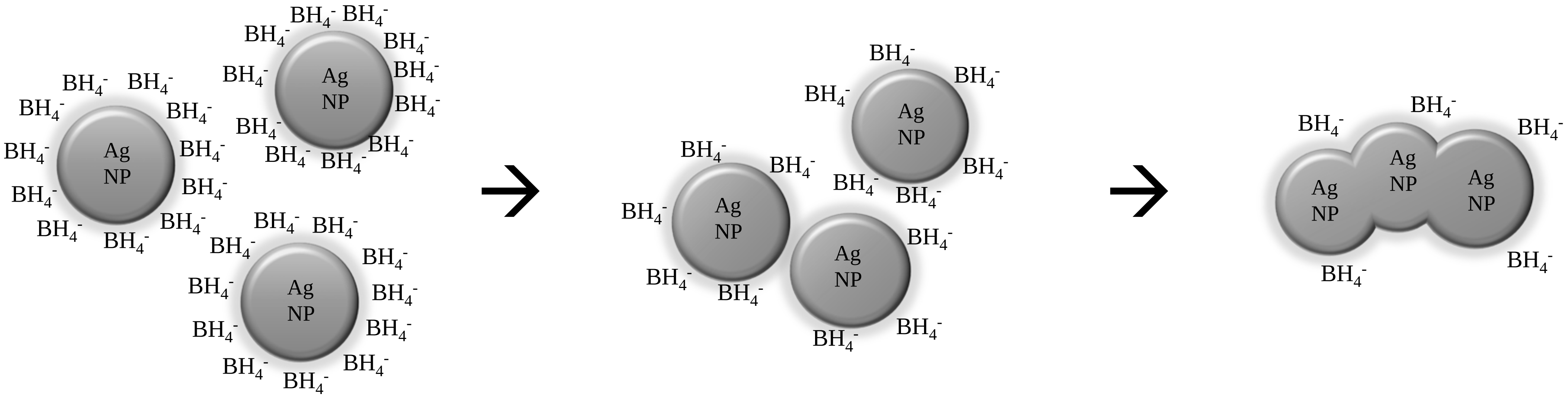
And the result….



90 Minutes



What Keeps the Particles Stable?

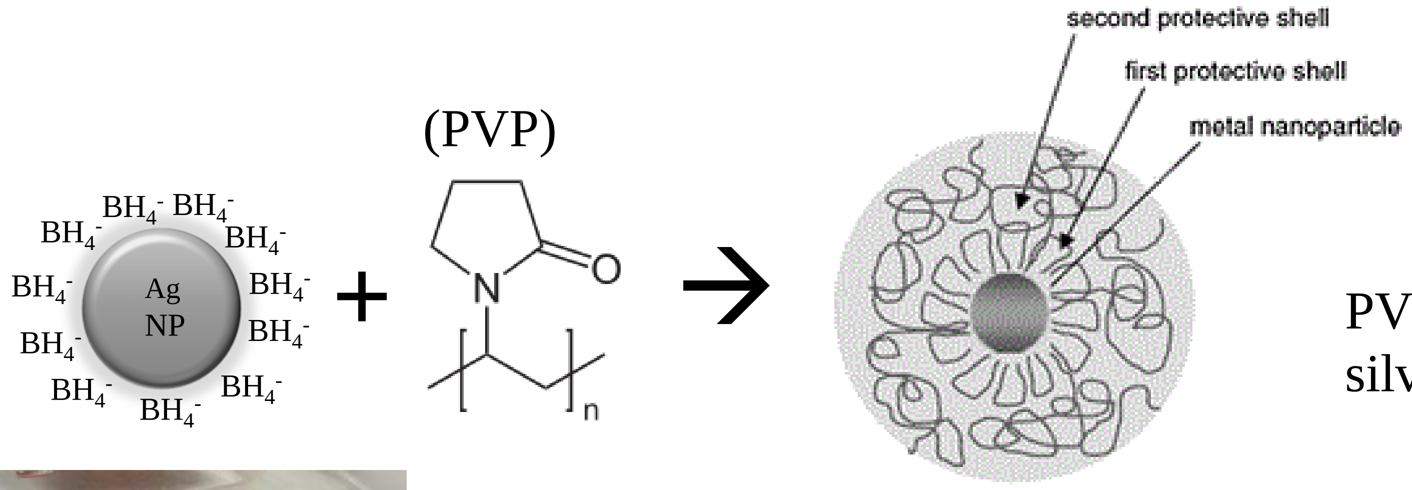


Maximum Time of Stability from Borohydride Repulsion alone: 90 minutes

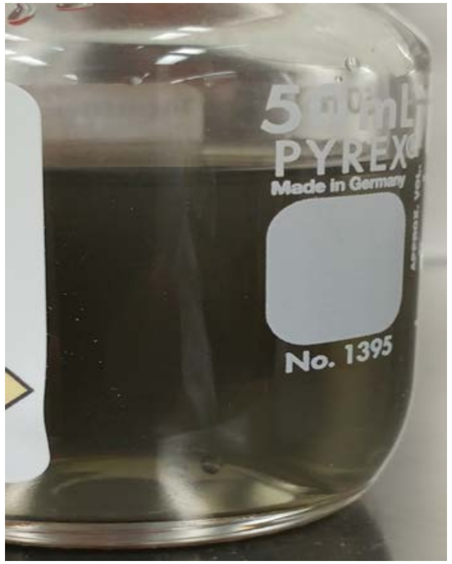
Something else needed to be added to extend life of solution

Addition of a Stabilizing Agent

Polyvinylpyrrolidone (PVP) is a water-soluble commonly used for stabilizing metal nanoparticles.



PVP is used for its ability to be removed from silver without changing surface chemistry

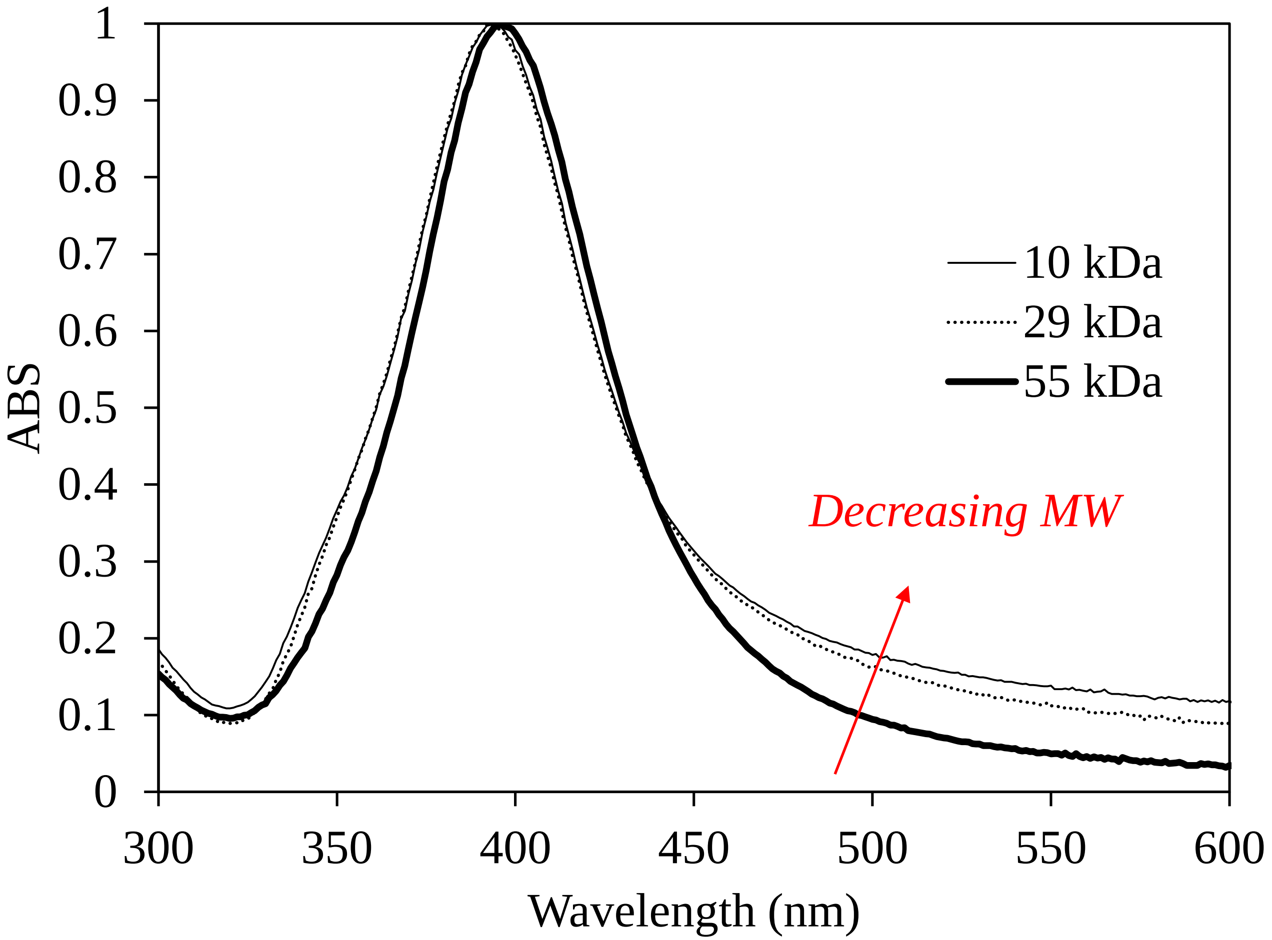


<u>Left:</u> Unstable Solution without PVP after 90 minutes

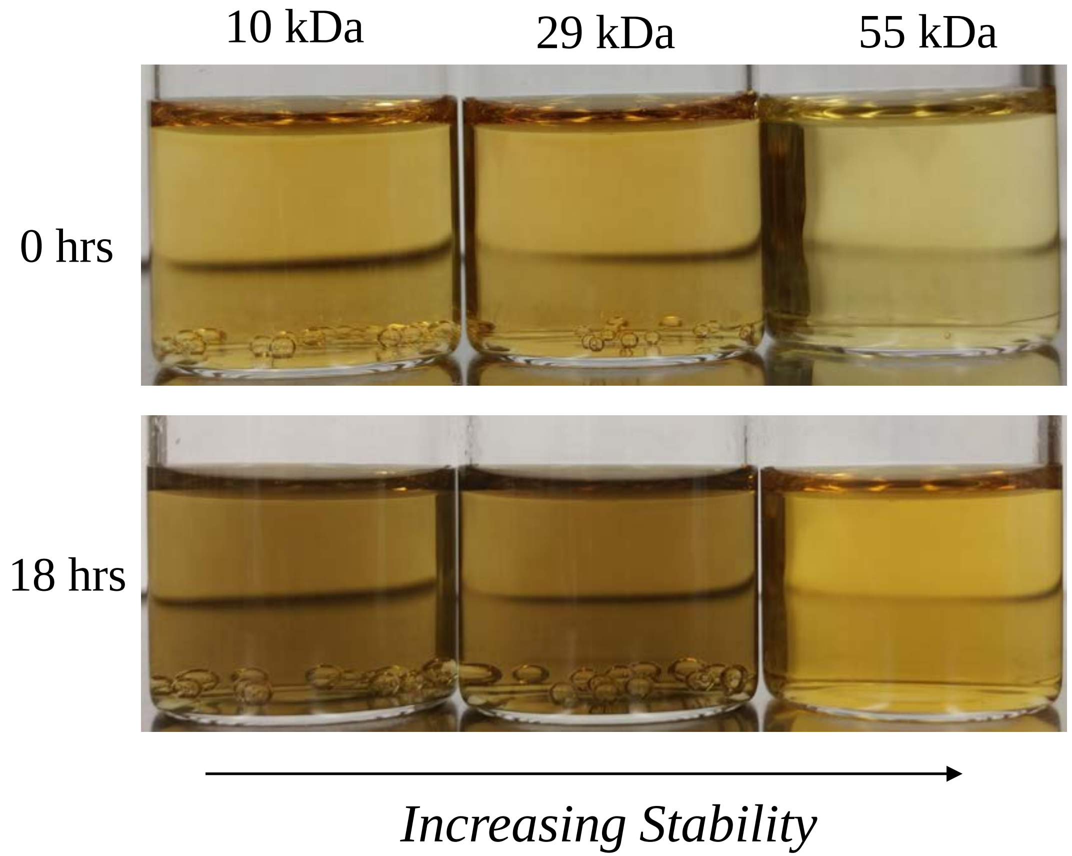
<u>Right:</u> Stable Solution with PVP after 3 weeks

Jia, C.-J.; Schüth, F. *Physical Chemistry Chemical Physics*2011, *13*(7), 2457.

Exploring the Effects of PVP Molecular Weight on Particle Stability

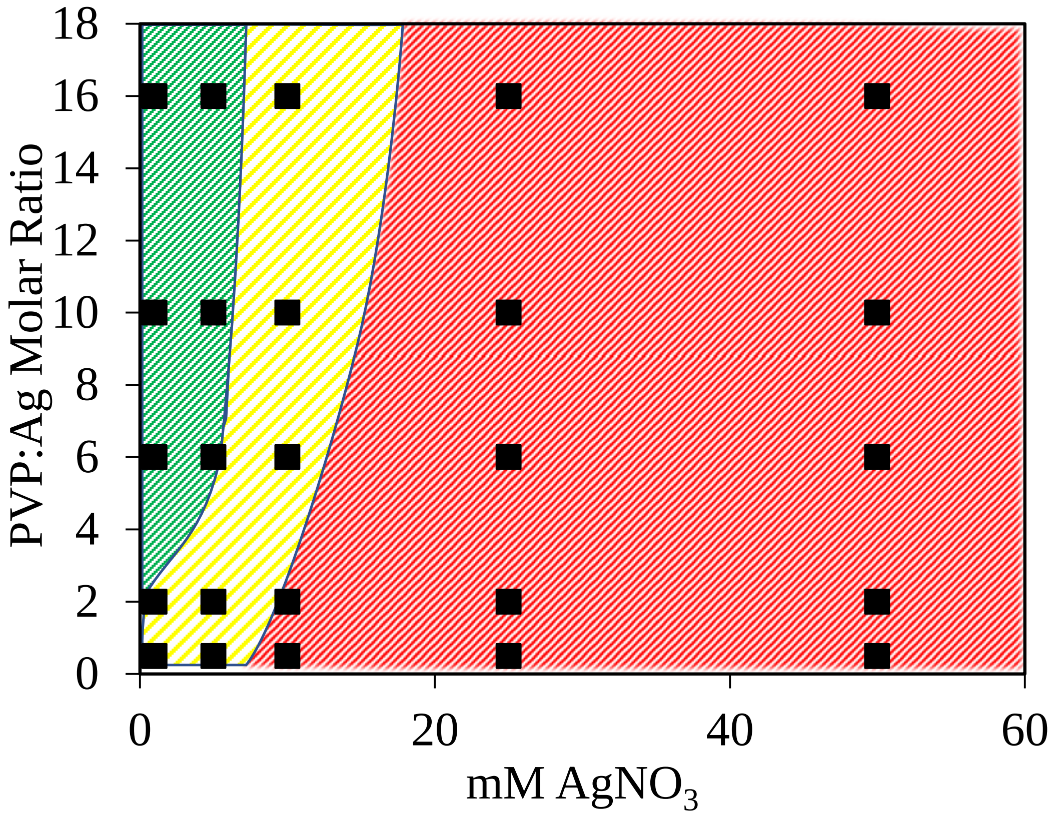


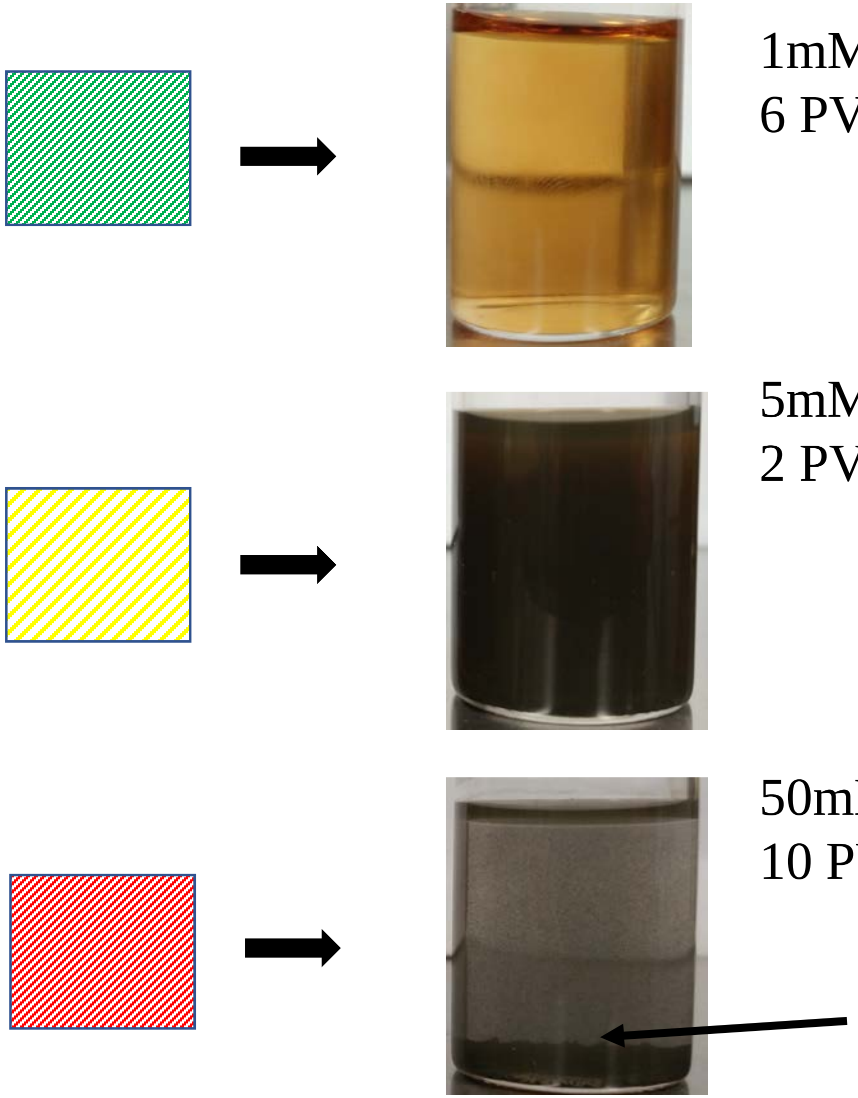
Molar Ratios of PVP:Ag Constant, varying MW



Due to the fast kinetics of this reduction reaction, high molecular weight PVP stabilizes the silver nanoparticles better than lower molecular weights.

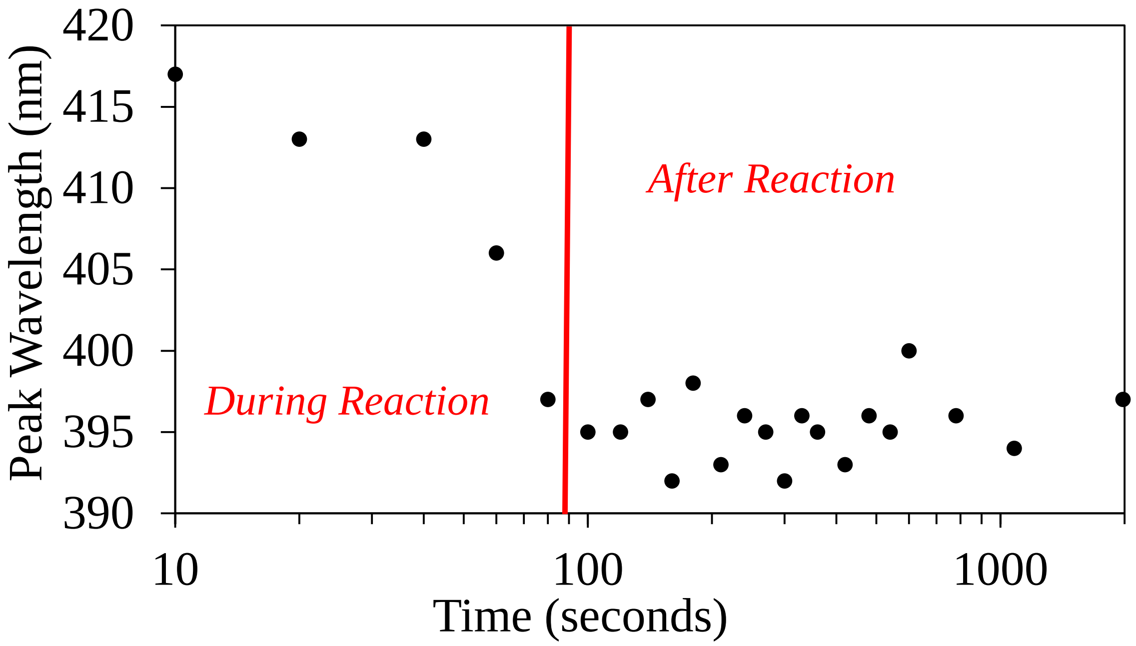
Process Diagram

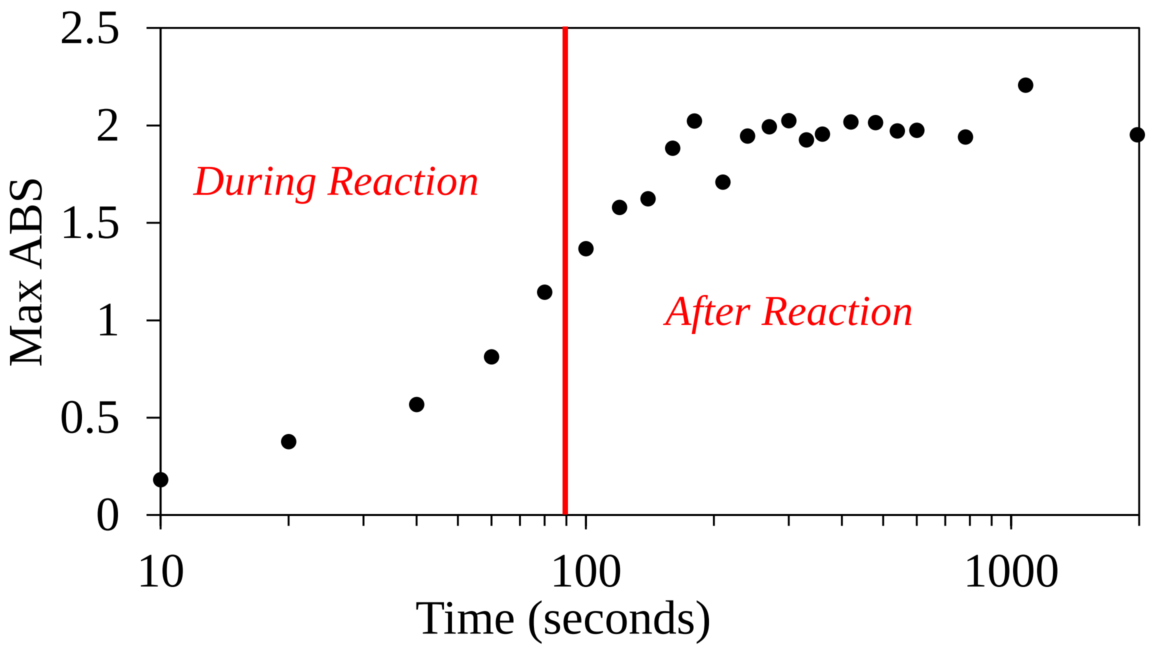




Increasing PVP:Ag molar ratio alone can not stabilize high concentration solutions.

Time Dependence of Shape Evolution



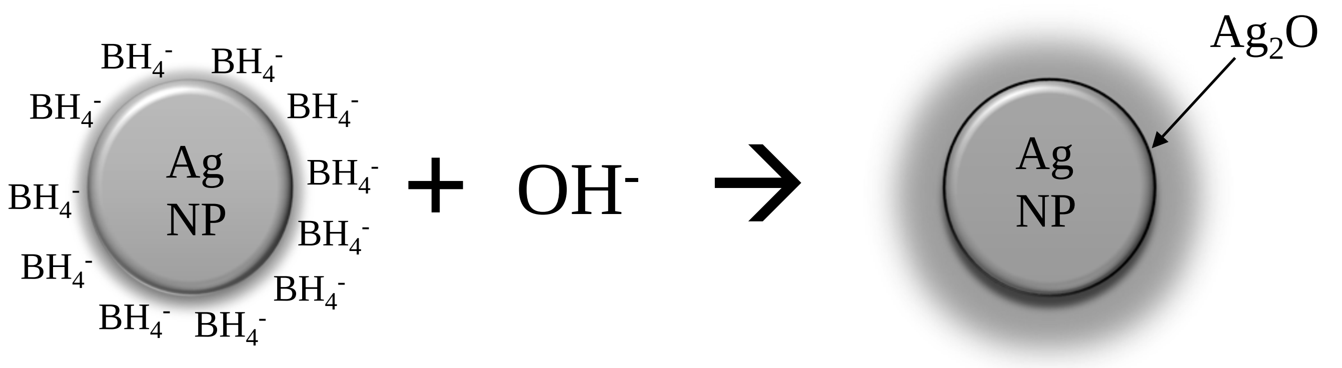


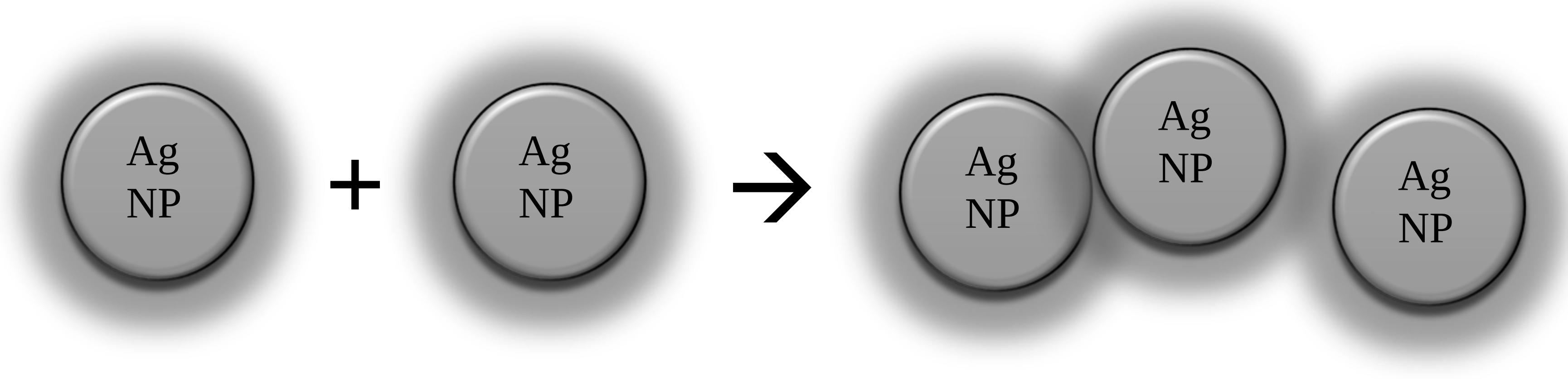
+18 hours

Stopping the reaction right after complete addition of silver nitrate can yield desired results

Reason for Shape Evolution

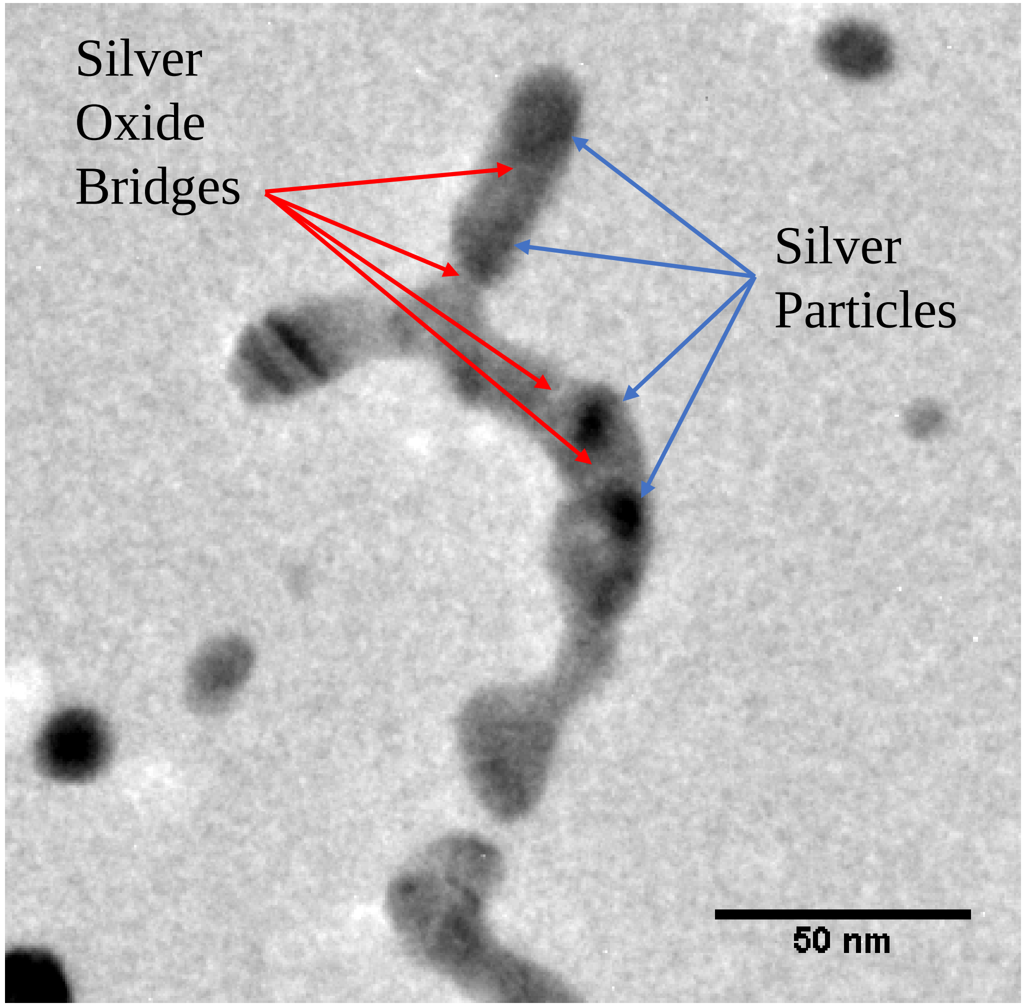
$$2Ag^{+} + 2OH^{-} \rightleftharpoons Ag_2O + H_2O$$

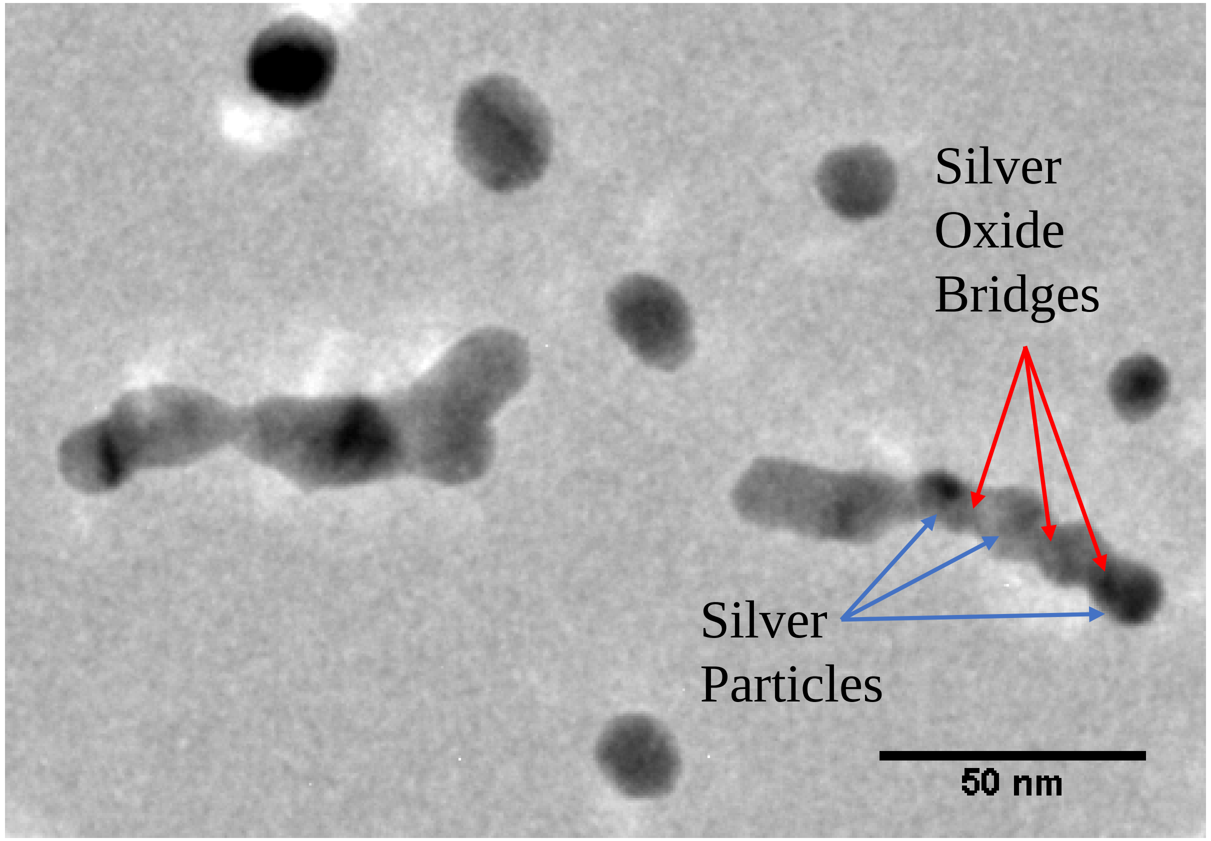




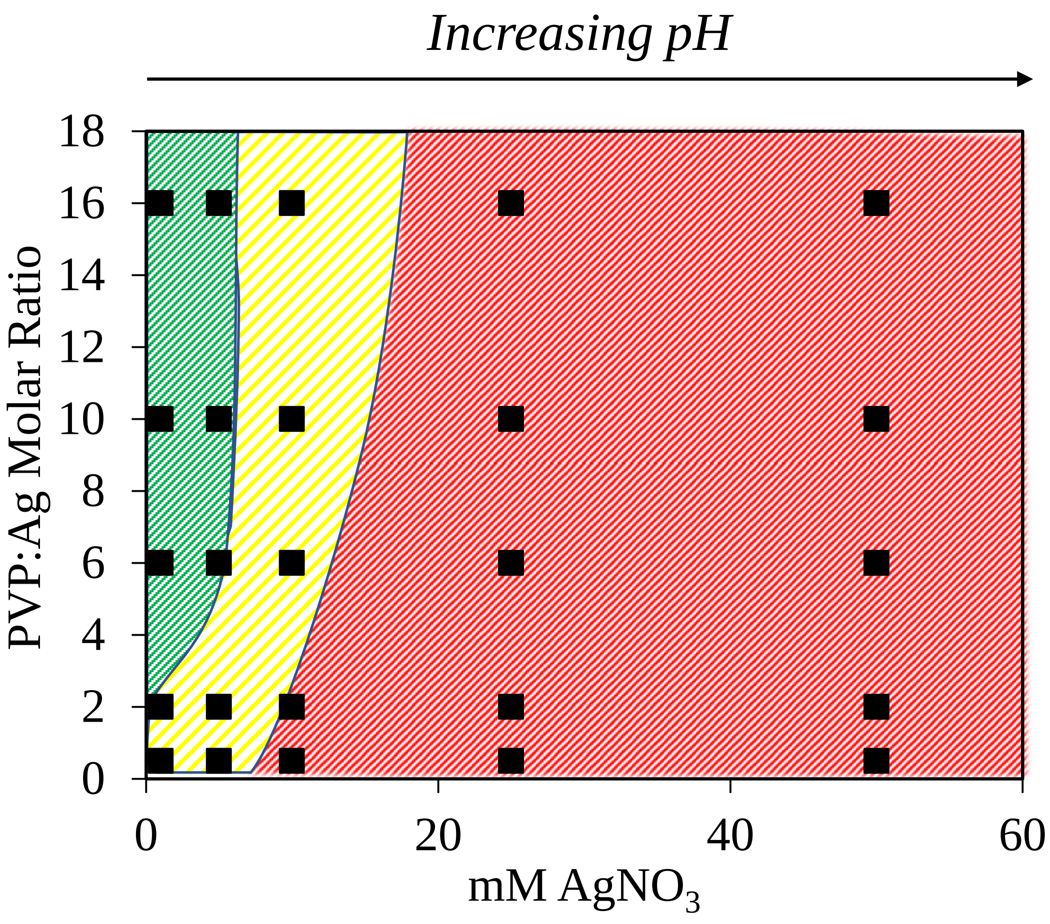
Reason for Shape Evolution

Shape Evolved, 10mM Silver Nanoparticle Solutions





Process Diagram



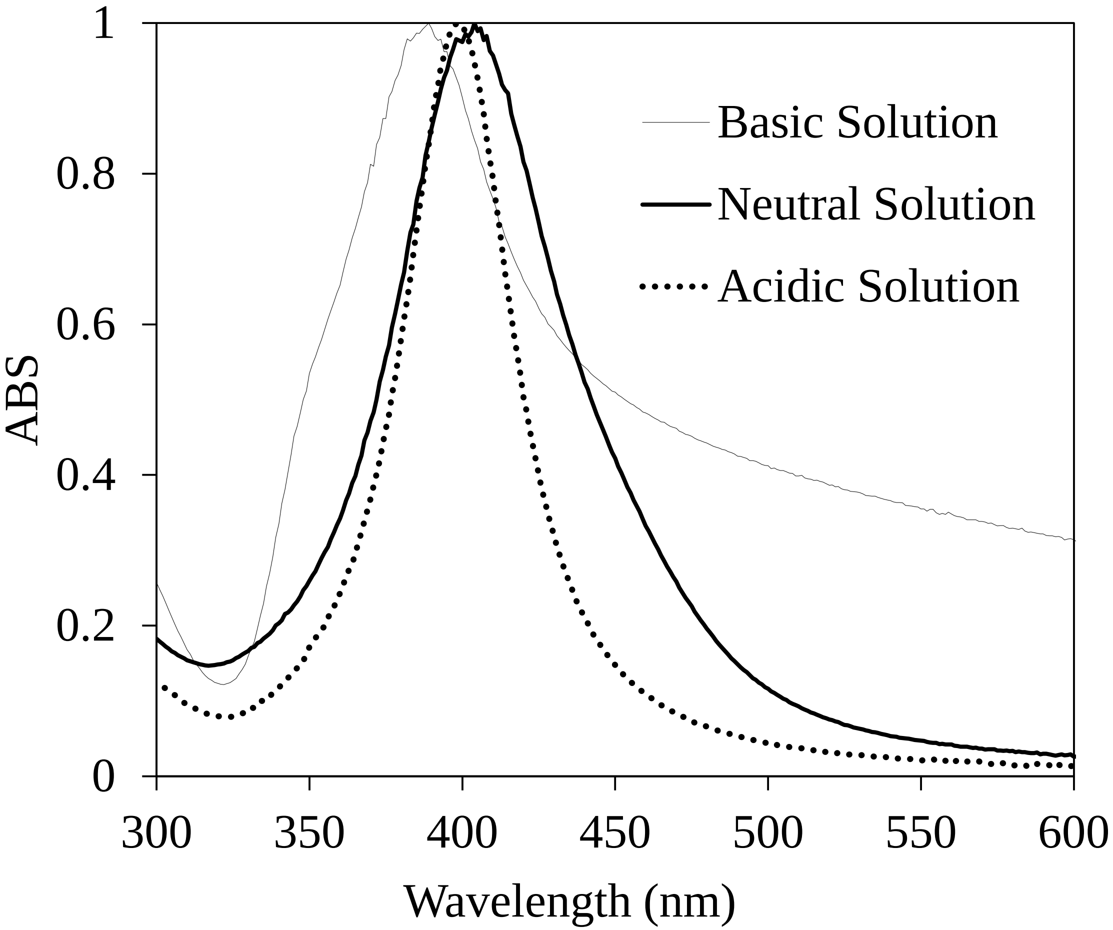
Silver Nitrate Concentration (mM)

PVP:Ag Molar Ratio

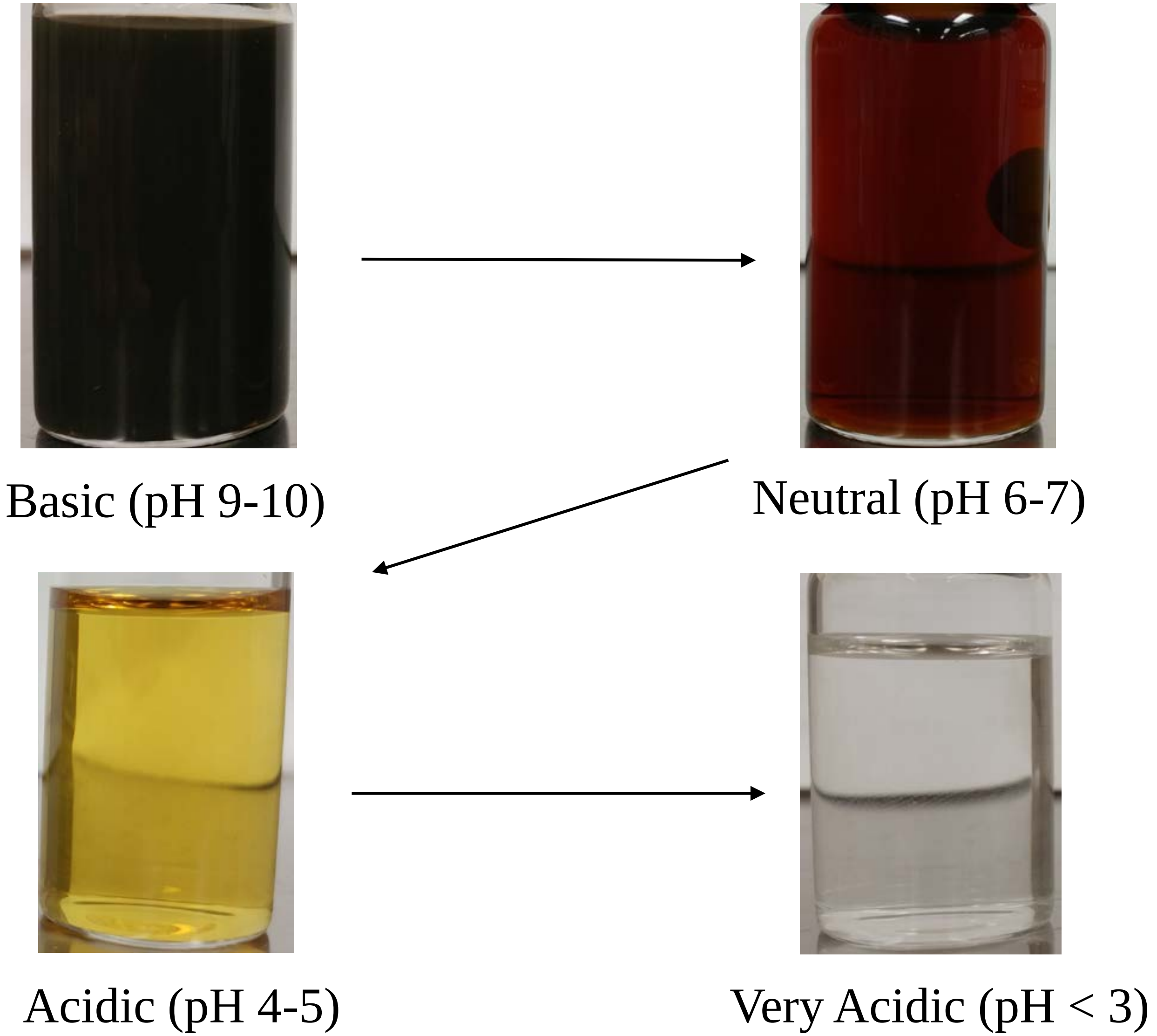
pH at Time 18 hrs (roughly)					
	1	**5**	**10**	**25**	**50**
16			9.61		
10	8.8	9.46	9.77	9.9	9.99
6	8.64	9.32	9.64	9.95	10.04
2	8.86	9.39	9.71	9.91	10.06
0.5	8.61	9.45	9.78	9.98	10.09

pH has an inverse correlation with particle stability

Quenching Reaction by pH Adjustment

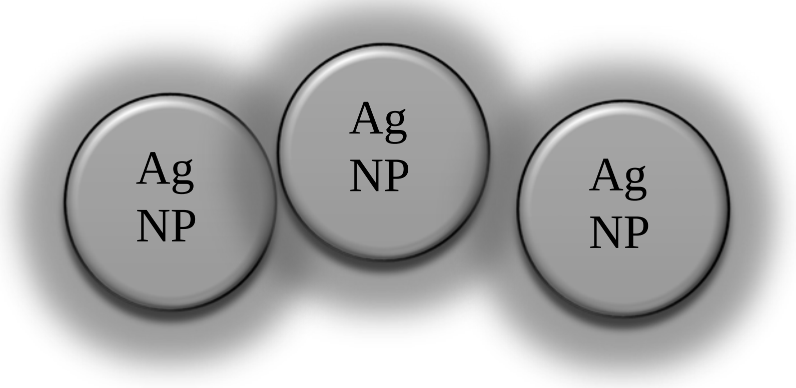


Decreasing pH increases monodispersity at the expense of particle concentration

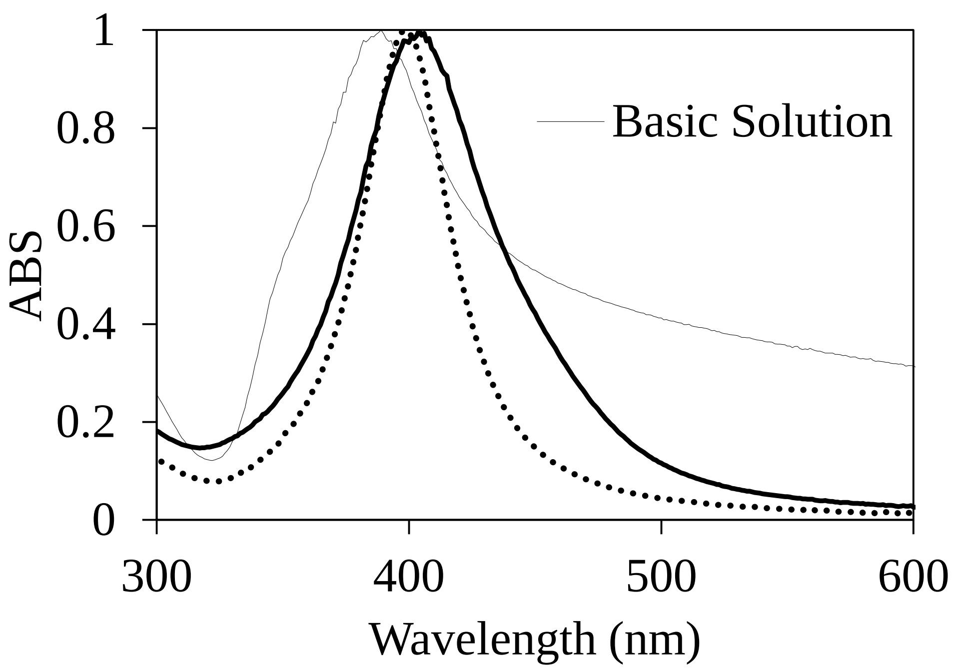


Conclusions

- Ionic repulsion can not provide stability, a stabilizing agent such as PVP is required
- Decreasing pH increases monodispersity at the expense of particle concentration
- Weak acidity (pH 6-7) will dissolve only Ag_2O, leaving a stable, monodispersed silver nanoparticle solution.



Reason for shape evolution over time



Stable monodispersed 10mM silver nanoparticle solution

Future Work

- Push past known concentration limits for production of silver nanoparticles
- Extract particles from water and redisperse in various solvents
- Test the electrical conductivity of these particles suspended in solution at the onset of electrical percolation

Acknowledgements

- Jeffrey Richards - Mentor
- Julie Borchers, Joe Dura – NCNR SURF Directors
- John Riley
- Mikala Shremshock

CHRNS
CENTER FOR HIGH RESOLUTION NEUTRON SCATTERING

NIST Center for Neutron Research