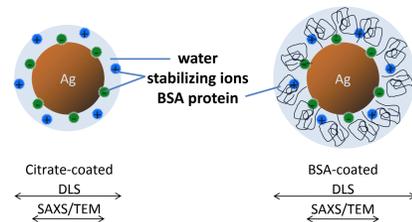


Introduction

Silver nanoparticles (AgNPs) are the focus of intense scientific research because they have unique biological and environmental properties that are not present in their elemental and bulk counterparts [1]. Unlike gold, elemental Ag is a natural biocide and, at the nanoscale, the chemical activity is amplified due to the increased ratio of surface to volume atoms. However, aqueous AgNPs are not inert, unlike gold; AgNPs agglomerate, precipitate, and dissolve in water if not carefully stabilized.

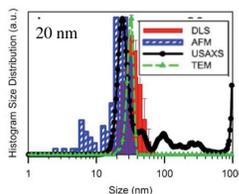
Dissolution of AgNPs is poorly understood, and at high acid concentrations (pH≈1, HCl stomach acid), typical protective coatings such as citrate and Polyvinylpyrrolidone (PVP) cannot protect the AgNPs from the acidic environment. To study AgNP dissolution at low pH, covalently bound capping agents such as bovine-serum albumin (BSA) and thiolated polyethyleneglycol (PEG) are needed.

In situ measurements of Ag NP dissolution were performed in nitric acid (HNO₃) to avoid AgCl precipitation in HCl (found in human stomach). We present results showing quantitative dissolution of BSA-, PEG-, and citrate-coated silver nanoparticles in HNO₃ down to pH 0.3 to explore how different coatings impact dissolution kinetics and intermediate particle morphologies formed during dissolution. Synchrotron-based small-angle X-ray scattering (SAXS), ultraviolet-visible extinction spectroscopy (UV-vis), dynamic light scattering (DLS), and transmission electron microscopy (TEM) were used to characterize the particles. This multidisciplinary measurement approach was crucial in quantifying the complex dissolution process for AgNPs at dilute concentrations.



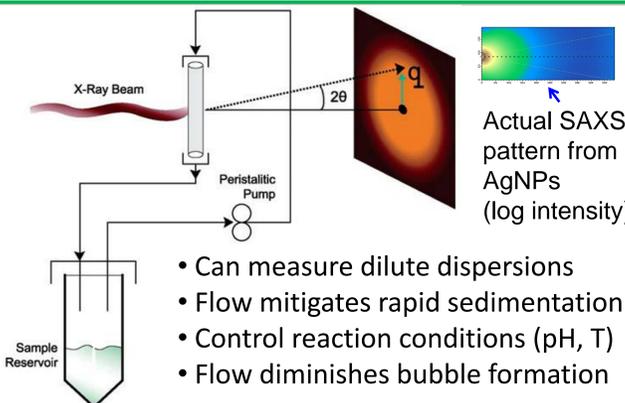
Key Measurements [3]

Attribute	UV-vis	DLS	TEM	SAXS
Diameter	core	core-shell	core	core
Range	1-100nm	10nm-10µm	>1nm	1nm-1µm
Polydispersity		Quantified mainly by SAXS		
<i>In-situ</i> ?	yes	yes	no	yes
Environment	dispersion	dispersion	substrate	dispersion
# NPs Measured	> 10 ¹³	> 10 ¹³	10 ² -10 ³	> 10 ¹³



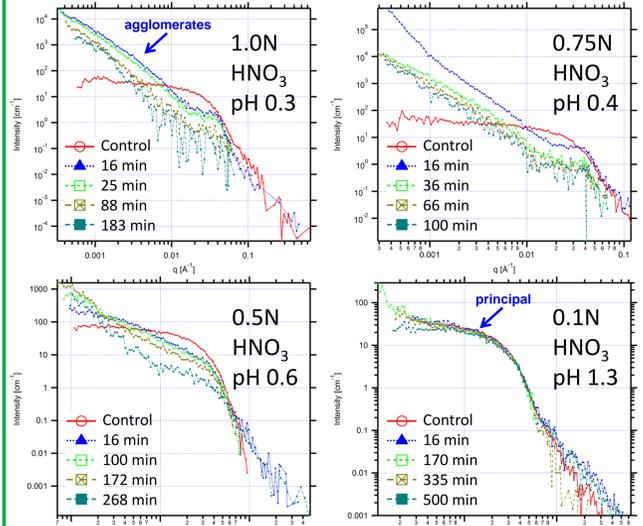
DLS, AFM USAXS and TEM all reveal different AgNP size distribution sampling. In this nominal 20 nm AgNP sample, all techniques detect the peak in the size distribution but the weighting clearly varies with technique. [3]

Flow Cell for *in situ* USAXS/SAXS¹



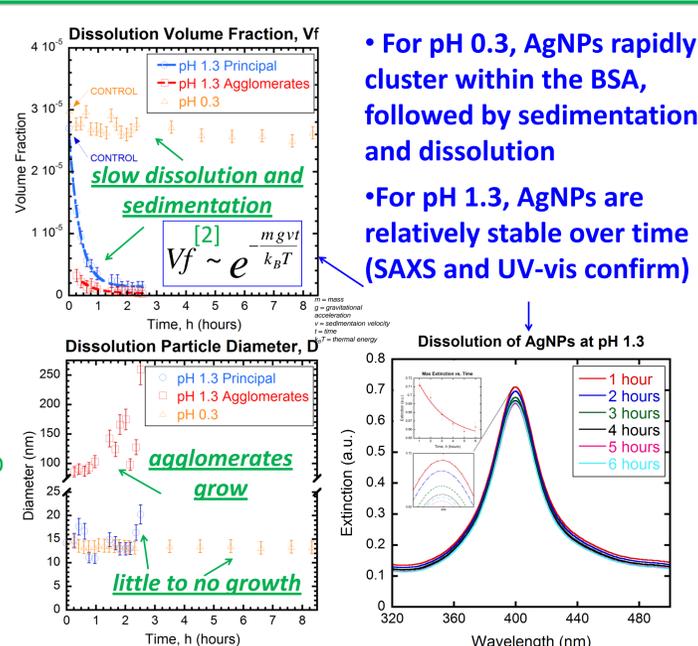
In situ USAXS Studies

Advanced Photon Source, Argonne National Lab, Sector 151D

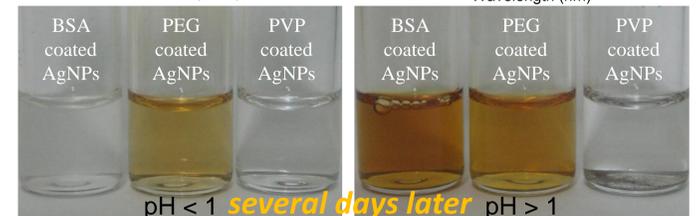


• pH 0.3, 0.4: AgNPs agglomerate (shoulder), sediment and dissolve
• pH 0.6: AgNPs agglomerate/dissolve, pH 1.3: AgNPs dissolve slowly

Dissolution of Silver Nanoparticles

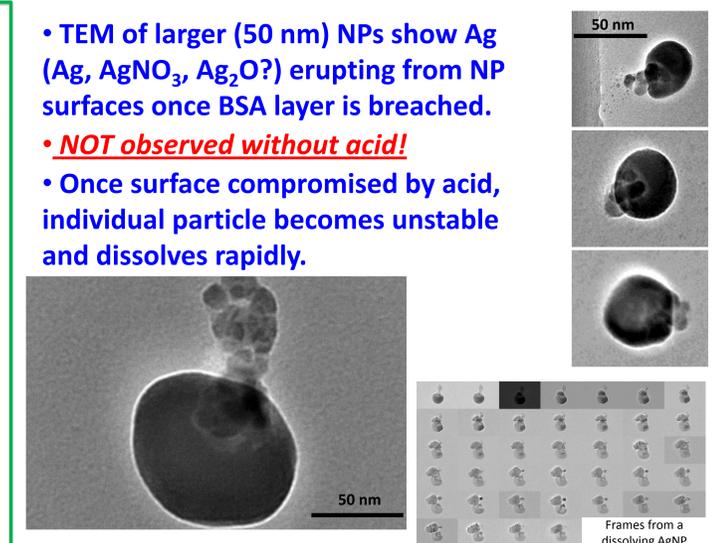


- For pH 0.3, AgNPs rapidly cluster within the BSA, followed by sedimentation and dissolution
- For pH 1.3, AgNPs are relatively stable over time (SAXS and UV-vis confirm)



BSA clusters several days later show AgNPs have fully dissolved!
Above pH 1, BSA and PEG protect AgNPs from dissolution very well, but they begin to fail at higher acid concentrations

Snapshots of Surface Rupture

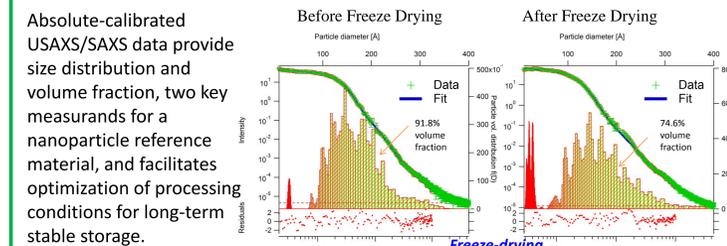


- TEM of larger (50 nm) NPs show Ag (Ag, AgNO₃, Ag₂O?) erupting from NP surfaces once BSA layer is breached.
- **NOT observed without acid!**
- Once surface compromised by acid, individual particle becomes unstable and dissolves rapidly.

Silver Nanoparticle RM (in development)

Problem: AgNPs are unstable at room temperature in water.

Solution: Freeze-dry material and reconstitute for use!



Freeze-drying preserves size distribution

CONCLUSIONS

- Coated AgNPs are stable against acid attack, unless the pH is below that for the coating molecule stability.
- For lower pH, dissolution/aggregation occurs, resulting in competing sedimentation/slow particle dissolution.
- SAXS, UV-vis, and DLS determine dissolution and aggregation rates at different acid concentrations.
- TEM shows how acid breaches a nanoparticle surface coating and initiates dissolution.

References:
[1] R.I. MacCuspie, A.J. Allen and V.A. Hackley; "Dispersion stabilization of silver nanoparticles in synthetic lung fluid studied under *in situ* conditions," *Nanotoxicology*, **5**, 140-156 (2011).
[2] C.P. Royall, R. van Roij, and A. van Blaaderen. "Extended Sedimentation Profiles in Charged Colloids: The Gravitational Length, Entropy, and Electrostatics," *J. Phys.: Condens. Matter*, **17** 2315-2326 (2005).
[3] R.I. MacCuspie, K. Rogers, M. Patra, Z. Suo, A.J. Allen, M.N. Martin and V.A. Hackley; "Challenges for physical characterization of silver nanoparticles under pristine and environmentally relevant conditions," *J. Environ. Monit.*, **13**, 1212-1226 (2011).

WORKING MODEL

