Supporting Information

Rapid Kinetics of Size and pH-Dependent Dissolution and Aggregation of Silver Nanoparticles in Simulated Gastric Fluid

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NTA Number Size and Total Concentration Measurements

The change in AgNP concentration (Figure S1) and diameter (Figure S2) for each SGF and neutral water over the experimental time period as measured by NTA. Initial concentration varied as each solution was created separately and it was difficult to always reproduce the exact same dissolution between experiments.



Figure S1. AgNP particle concentration loss over time for each AgNP under varying SGF pH and neutral water (pH 6).



Figure S2. AgNP particle growth over time for each AgNP under varying SGF pH and neutral water (pH 6).

The image plots for the neutral water experiments are provided in Figure S3. These images plots show that the number concentration, as well as the mode and shape of the size distribution is constant for the control group during the experiment.



Figure S3. Image plots for Citrate 20, PVP 20, Citrate 110, and PVP 110 showing no change in particulate size and concentration over time in neutral water. The grey bar in each graph indicates time in which there was no sizing data.

Size dependent dissolution: Ostwald-Freundlich calculations

The Ostwald-Freundlich Relation is used to determine the size dependent dissolution for AgNP. The relation is as follows:

$$S_r = S_{bulk} \times e^{(\frac{2\gamma V_m}{RT \times r})}$$

where S_r is the AgNP solubility of radius (r), S_{bulk} is the solubility of silver with a flat surface, γ is the AgNP surface tension, V_m is AgNP molar volume, R is the gas constant, and T is the temperature.¹ Our calculations only take into account the radius of the particles and not the respective surface coatings or solution pH. Results indicate that smaller, 20 nm, particles will dissolve at a faster rate than 110 nm particles (Figure S4).



Figure S4. Ostwald-Freundlich relation determined for initial particle sizes for all AgNP particles. The range indicates the upper and lower surface tension values.

Comparison of aggregation kinetics with previous literature

To compare our particle growth rate calculations to literature values, calculations from Tai et al.² were used to determine the lumped aggregation rate constant (log(k_D)) for each AgNP in SGF and compared the Citrate 20 nm in nitric acid measured by Tai et al. Results indicate that there is greater aggregation for SGF with HCl and NaCl that for HNO₃, even at higher pH representative of the fed (and thus slightly buffered) stomach.



Figure S5. Lumped aggregation rate constant from this work compared to that measured in previous studies.

AgNP Mass Calculations

The change in total particulate mass determined from each AgNP size distribution over the course of each experiment in SGF and water. The PVP 20 show an overall increase in total mass at pH 4.5, though the reason for this increase is not fully understood.



Figure S6. Total particulate mass determined from each AgNP size distribution over the course of each experiment in SGF and water. Linear fits were used to determine the rate with negative values indicating decrease in mass and positive values are increases in total mass.

Additional SEM images of AgNP

Representative SEM images of AgNP in neutral water during particle characterization are presented in figure S7. The Citrate 20, PVP 20, and PVP 110 were all collected in dark field, while Citrate 110 was collected in bright field.



Figure S7. SEM images collected for each AgNP in neutral water solutions.

References

 Ma, R.; Levard, C.; Marinakos, S. M.; Cheng, Y. W.; Liu, J.; Michel, F. M.; Brown, G.
E.; Lowry, G. V., Size-Controlled Dissolution of Organic-Coated Silver Nanoparticles. *Environ. Sci. Technol.* 2012, *46*, 752-759.

 Tai, J. T.; Lai, C. S.; Ho, H. C.; Yeh, Y. S.; Wang, H. F.; Ho, R. M.; Tsai, D. H., Protein Silver Nanoparticle Interactions to Colloidal Stability in Acidic Environments. *Langmuir* 2014, *30*, 12755-12764.