Electronic Supplementary Material (ESI) for Nanoscale.

Electronic supplementary information for:

Comparing Sulfidation Kinetics of Silver Nanoparticles in Simulated Media using Direct and Indirect Measurement Methods

Jingyu Liu, Fan Zhang, Andrew Allen, Aaron C. Johnston-Peck and John Pettibone

Sulfide Concentration Analysis by Ion Selective Electrode (ISE) and Direct Calibration and Analyte Subtraction Method

In direct calibration approach, a sulfide antioxidant buffer (SAOB) is added to prevent sulfide from oxidation and provide stable basic pH. The electrode responses are directly to free sulfide, where the voltage (*E*) is function of sulfide concentration:

$$E = E^{'} - \frac{RT}{2F}\ln\left[HS^{-}\right] = E^{'} - 0.029\log_{10}\left[HS^{-}\right] \qquad \text{Eq. S1}$$

where *E'* at given temperature and pH, *R* is the universal gas constant, *T* is the temperature in kelvin, *F* is the Faraday constant, [HS$^-$] is sulfide concentration.

In analyte subtraction approach, know amounts of Ag$^+$ (as in AgNO$_3$) is added into sulfide containing samples to quench the sulfidation reaction (sulfide is consumed rapidly by Ag$^+$). Consequently, sulfide concentration is derived from the change of Ag$^+$ content. Because Ag$^+$ is added in excess to sulfide, the electrode response is to Ag$^+$ and the voltage (E) is function of Ag$^+$ concentration:

$$E = E^{'} + \frac{RT}{F}\ln\left[Ag^{+}\right] = E^{'} + 0.059\log_{10}\left[Ag^{+}\right] \qquad \text{Eq. S2}$$

The difference of Ag$^+$ before and after spiked into sulfide samples is then used to calculate sulfide concentration based on stoichiometric reaction between Ag$^+$ and sulfide $2Ag^{+} + HS^{-} \rightarrow Ag_2S + H^{+}$.

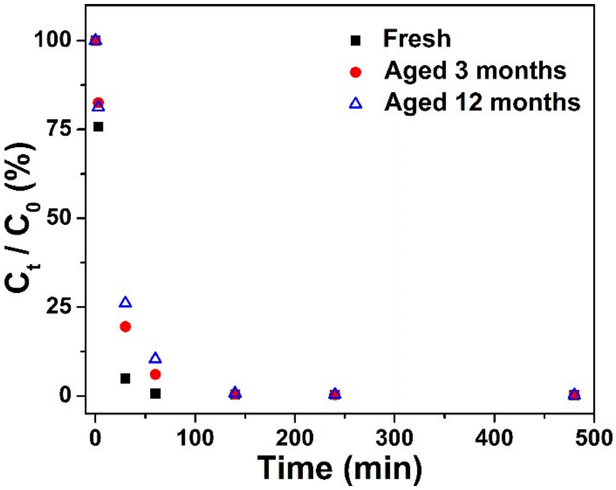

Figure S1. Sulfide depletion kinetics in Na$_2$S/FA mixture as a function of FA aging, showing sulfide decrease is most prominent by interreacting with fresh FA. The concentrations of Na$_2$S and

FA used 6.5 mM and 5,000 mg L^{-1}, respectively. The fresh FA stock solution at concentration of 50,000 mg L^{-1} were prepared by resuspending FA powder in water 15 h ahead of use, followed by rotation overnight to promote dissolution. The aged FA stocks were kept in glass vials protected from the light for 3 months and 12 months upon resuspension. ISE measurement used the direct calibration approach. Data fitting using first order reaction gives rate constants of 0.096 min^{-1}, (0.055 ± 0.002) min^{-1} to (0.045 ± 0.004) min^{-1} for fresh, 3 months-aged, and 12 months-aged FA, respectively. For comparison from Fig. 1B in the main text, the sulfide consumption rate in freshly prepared FA was (0.096 ± 0.002) $min^{-1,}$ compared to (0.045 ± 0.004) min^{-1} for FA aged for 12 months. In contrast, freshly prepared HA reacted slower with sulfide (0.012 ± 0.001) min^{-1} than aged HA, (0.032 ± 0.003) min^{-1}.

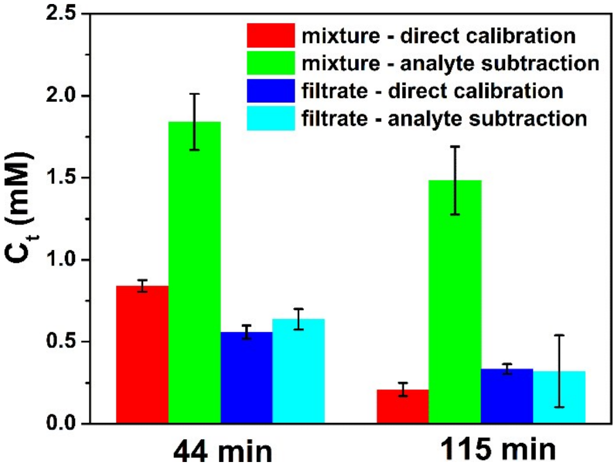

Figure S2. Comparison of sulfide measurements in Na_2S/FA mixtures and clear FA free filtrates. The experiment was initiated by adding Na_2S into a pH adjusted fresh FA solution in MHRW. At 44 min and 115 min, aliquots were taken and filtered through Amicon-4 centrifugal ultrafiltration tubes (molecular weight cutoff 3K, 14,000 rpm for 20 min) to remove the FA and FA bound sulfide. The remaining sulfide in FA free filtrates were determined with ISE using both the direct and analyte subtraction approach. Meanwhile, the sulfide concentrations in the unfiltered mixtures were analyzed by ISE using both sulfide direct calibration and analyte subtraction methods. The sulfide concentrations in the filtrates were lower than the sulfide level measured in mixtures by the analyte subtraction method, but was comparable to sulfide level in mixtures measured by the direct calibration method. This result suggests the observed discrepancy of ISE measurements by these two methods in the Na_2S/FA mixture is attributed to the formation of FA bound active sulfide species.

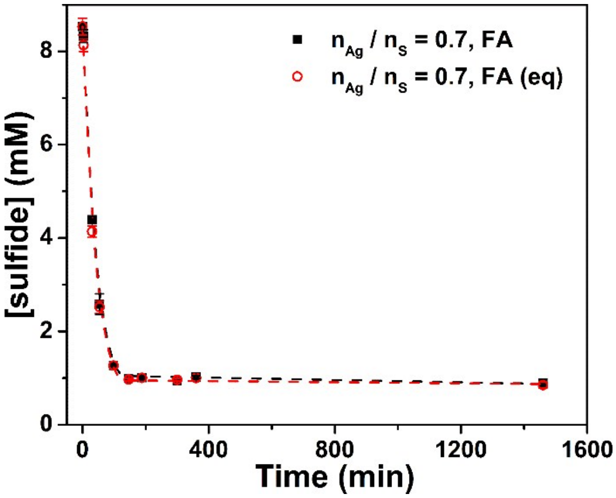

Figure S3. Sulfide depletion kinetics for AgNP sulfidation in the presence of FA, showing AgNP pre-adsorbed with FA has no effect on sulfide depletion rate. Sulfide were measured by ISE *via* the analyte subtraction approach. AgNPs were mixed with pH adjusted FA in MHRW, and the Na_2S were added at the last to initiate the reaction. The incubation time of AgNPs in FA was adjusted to be 10-30 s (black square symbol, n = 2) and 15 h (red hollow sphere symbol, n =2) to evaluate the effect of surface FA adsorption. The final concentrations of AgNP, FA and Na_2S were 1,400 mg L^{-1}, 7,000 mg L^{-1}, and 9.1 mM, respectively. The dashed lines show fitting using a two-stage first order kinetic law for the fast and slow consumption of sulfide by AgNPs and solution oxidation, respectively[1]. The error bars give the standard deviation of duplicate experiments.

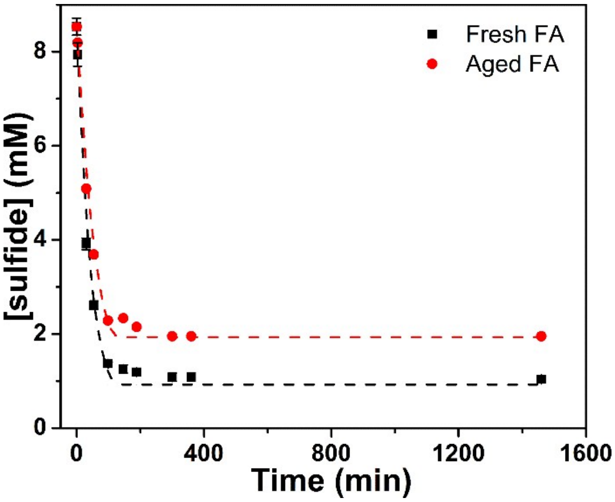

Figure S4. Sulfide depletion kinetics in Na_2S/FA mixture as a function of FA aging, showing reduced sulfide depletion in aged FA. The final concentrations of Na_2S and FA and were 9.1 mM, and 7,000 mg L^{-1}, respectively. The fresh FA stock solution at concentration of 50 mg mL^{-1} were prepared by dissolving FA powder in water 15 h ahead of use, followed by subsequent rotation overnight to promote dissolution. The aged FA stocks were kept in glass vials protected from the light for 2 months. ISE measurements used the analyte subtraction method. The error bars of sulfide depletion in fresh FA give standard deviations of duplicate experiments. The dashed lines show fitting using a two-stage first order kinetic law for the fast and slow consumption of sulfide by AgNPs and solution oxidation, respectively.[1]

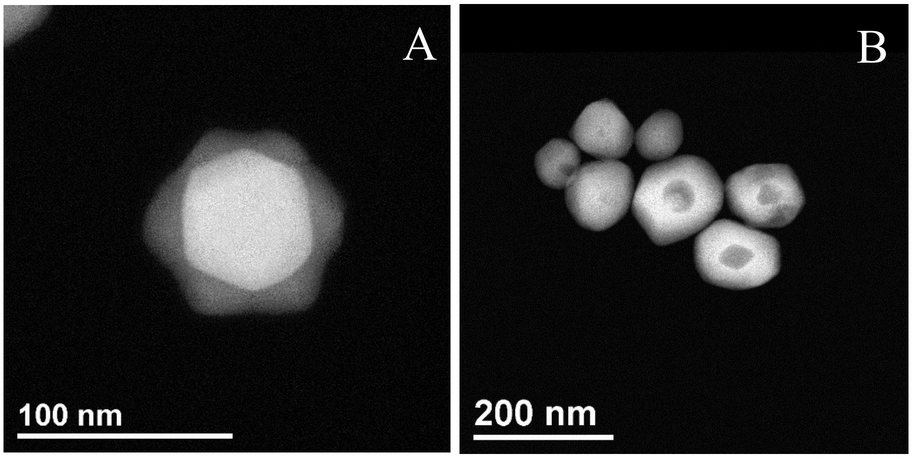

Figure S5. TEM images of the sulfidated products resulting from HS^- and A) PVP-coated AgNPs and B) citrate coated AgNPs at $t = 24$ h, which is past the asymptote observed with diffraction and ISE measurements. Clear differences in the stability and structure were observed. Only Ag_2S and Ag^0 were detected in the NPs, excluding other common Ag precipitates in the presence of carbonates and chloride.

1 Liu, J.Y.; Pennell, K.G.; Hurt, R.H. Kinetics and Mechanisms of Nanosilver Oxysulfidation. *Environmental Science & Technology* **2011**, (45), 7345-7353; 10.1021/es201539s