

## Supporting Information

# **Silver Sulfide Nanoparticles in Aqueous Environments: Formation, Transformation and Toxicity**

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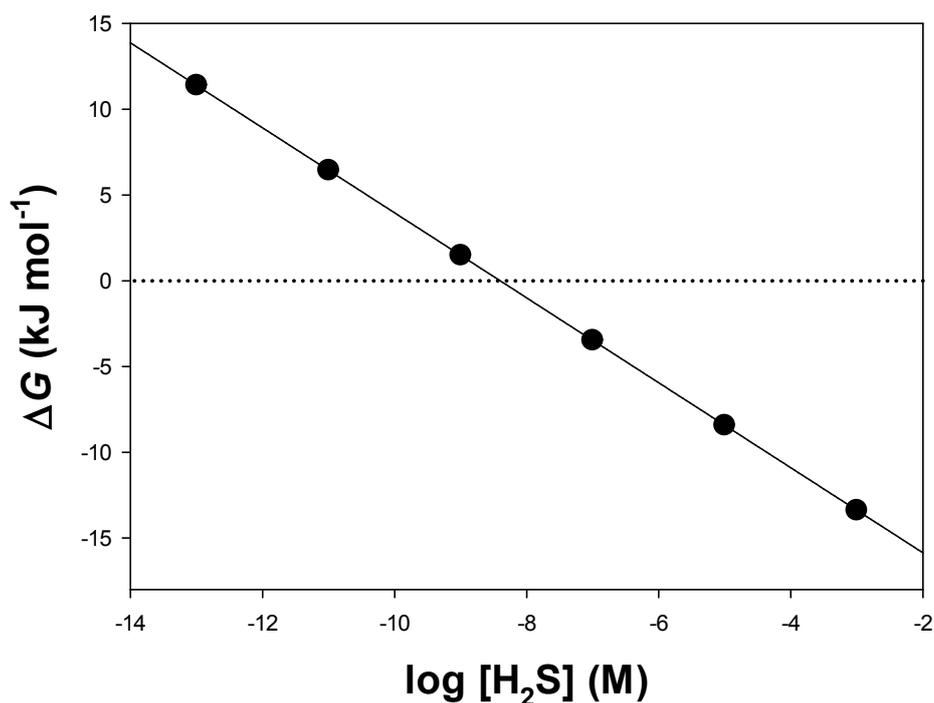
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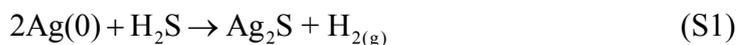
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**Figure S1.** Calculation of  $\Delta G$  for the reaction between  $\text{Ag}(0)$  and  $\text{H}_2\text{S}$  as a function of  $[\text{H}_2\text{S}]$ .

The reaction between  $\text{Ag}(0)$  and sulfide may occur as following (Eq. S1),



At equilibrium,

$$\log K = \log Q = -\log[\text{H}_2\text{S}_{(\text{aq})}] + \log[\text{H}_{2(\text{aq})}] \quad (\text{S2})$$

where  $\log K = 2.0327$  and  $[\text{H}_{2(\text{aq})}]$  normally in water is  $4.29 \times 10^{-7}$  M at  $25^\circ\text{C}$ , then

$$[\text{H}_2\text{S}_{(\text{aq})}] = 3.98 \times 10^{-9} \text{ M} \quad (\text{S3})$$

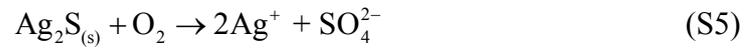
As such, when the concentration of  $\text{H}_2\text{S}_{(\text{aq})}$  is over  $\sim 4$  nM, the reaction of  $\text{Ag}(0)$  with  $\text{H}_2\text{S}$  under anoxic environment is favored.

$\Delta G$  in Figure S1 can be calculated as a function of  $[\text{H}_2\text{S}]$ ,

$$\Delta G = 2.3RT \log(Q / K) \quad (\text{S9})$$

where  $T = 298$  K,  $R = 8.314$  J K<sup>-1</sup> mol<sup>-1</sup>,  $K = 2.0327$  and  $[\text{H}_{2(\text{aq})}] = 4.29 \times 10^{-7}$  M at  $25^\circ\text{C}$ .

The oxygenation of Ag<sub>2</sub>S may occur as following (Eq. S5):



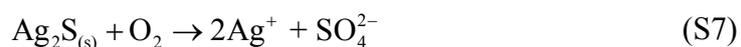
At equilibrium,

$$\log K = -\log[\text{O}_{2(\text{aq})}] + 2\log[\text{Ag}^+] + [\text{SO}_4^{2-}] \quad (\text{S6})$$

where  $\log K = 102.28$  and  $[\text{O}_{2(\text{aq})}] = 0.25$  mM under air-saturated conditions at 25 °C.

According to Eq. S4,  $\Delta G$  is always  $<0$  under oxic environments where concentrations of  $\text{Ag}^+$  and  $\text{SO}_4^{2-}$  are in the typical concentrations.

The oxygenation of Ag<sub>2</sub>S may occur as following (Eq. S7):



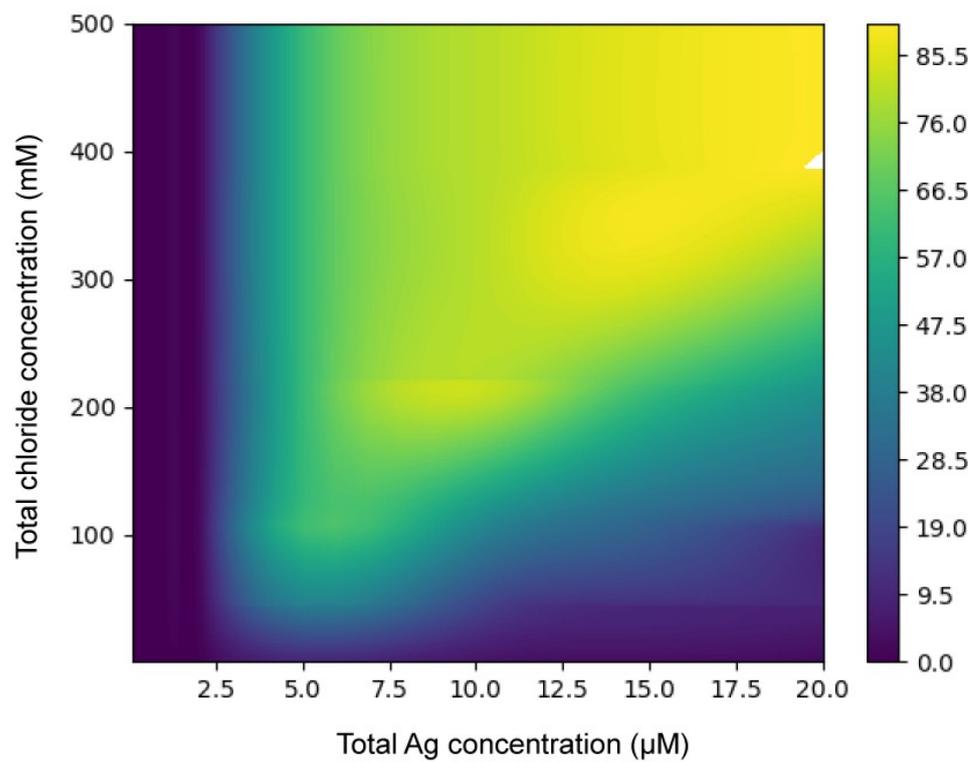
The reaction quotient ( $Q$ ) is:

$$\log Q = -\log[\text{O}_{2(\text{aq})}] + 2\log[\text{Ag}^+] + [\text{SO}_4^{2-}] \quad (\text{S8})$$

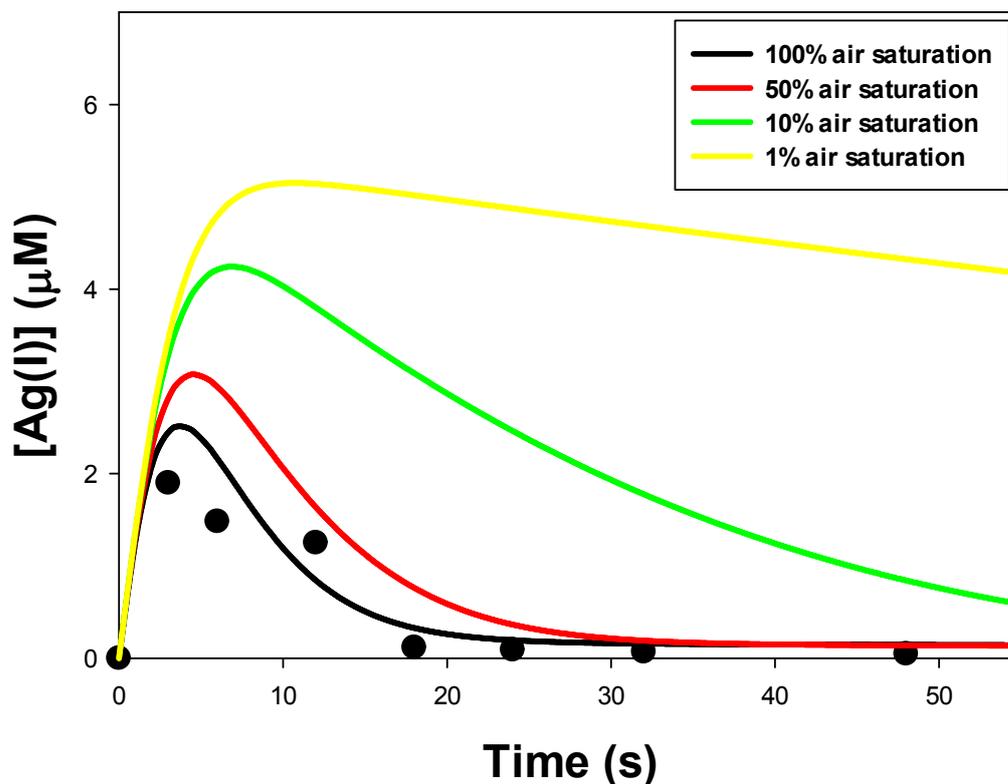
where  $[\text{O}_{2(\text{aq})}] = 0.25$  mM under air-saturated conditions. Comparison of  $Q$  (actual composition) with the value of  $K$  (equilibrium composition) determines if the reaction can occur ( $\Delta G < 0$ ):

$$\Delta G = 2.3RT \log(Q / K) \quad (\text{S9})$$

where at 25 °C  $\log K = 102.28$ ;  $T = 298$  K and  $R = 8.314$  J K<sup>-1</sup> mol<sup>-1</sup>. As such,  $\Delta G < 0$  under oxic environments where concentrations of Ag<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> are in the range of micromolar to millimolar.



**Figure S2.** Thermodynamic speciation calculation showing % Ag present as dissolved AgCl complexes for varying total Ag(I) and Cl<sup>-</sup> concentrations at pH 8.0 in the presence of 1 μM of total sulfide.



**Figure S3.** Effect of dissolved oxygen on light irradiation induced dissolution kinetics of  $\text{Ag}_2\text{S}$ -NPs in the presence of  $\text{Fe(III)}$ . Symbols are experimental data from Li et al<sup>1</sup>; Lines in Figure S1 are the model fittings based on reaction scheme I (Table 1) under various air saturation conditions. Experimental conditions:  $[\text{Ag}_2\text{S-NPs}]_0 = 5.0 \text{ mg L}^{-1}$ ;  $[\text{Fe(III)}]_0 = 2.0 \text{ mg L}^{-1}$ ;  $\text{pH} = 5.0$ . Reprinted with permission from the American Chemical Society.

### References

1. Li, L. X. Y.; Zhou, Q. F.; Geng, F. L.; Wang, Y. W.; Jiang, G. B., Formation of nanosilver from silver sulfide nanoparticles in natural waters by photoinduced  $\text{Fe(II, III)}$  redox cycling. *Environ. Sci. Technol.* **2016**, *50*, (24), 13342-13350.