

## Supplementary material

### The concentration-dependent behaviour of nanoparticles

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### Transmission electron microscopy (TEM)

TEM analyses were performed using a Tecnai F20 Field Emission gun (FEG) transmission electron microscope. Samples were prepared by adopting and applying the recently developed fully quantitative sample preparation protocol developed for atomic force microscopy (AFM).<sup>[1]</sup> Suspension of citrate coated gold nanoparticles (cit-Au NPs) (1–20  $\mu\text{g L}^{-1}$ ) were deposited on TEM grids by ultracentrifugation of cit-Au NP suspensions on a carbon coated TEM grid at 150 000g, a force sufficient to deposit all Au NPs greater than 5 nm given the sample conditions. The number of Au NPs forming aggregates were counted manually and are presented in Fig. 1d.

### Dissolution analysis

The absorbance of poly(vinylpyrrolidinone) (PVP)-Ag NP suspensions at two different concentrations (~100 and 1000  $\mu\text{g L}^{-1}$ ) in seawater was monitored systematically over a period of one month using a UV-Vis spectrophotometer (UV-2600, Shimatzu Co., Kyoto, Japan). PVP-Ag NPs were mixed with seawater (100 mL) and were left at room temperature for 14 days. Aliquots of 10 mL were withdrawn at different time intervals for UV-Vis measurement. Dissolution of PVP-Ag NPs was monitored by UV-Vis absorbance at ~400 nm. As PVP-Ag NPs are sterically stabilised and therefore do not undergo aggregation in seawater, any reduction in the UV-Vis absorbance is attributed to NP dissolution.<sup>[2]</sup>

The dissolved Ag fractions were calculated as:

$$\text{Dissolved Ag fraction} = \frac{\text{UV}_{400t_0} - \text{UV}_{400t}}{\text{UV}_{400t_0}} \quad (\text{S1})$$

where  $\text{UV}_{400t_0}$  and  $\text{UV}_{400t}$  are the UV-Vis absorbance of Ag NPs in seawater at the beginning of the dissolution experiment and at different time points respectively.

The data were then fitted with a double exponent dissolution model, which is essentially an empirically derived equation describing the different parts of the dissolution curve of a dissolving solid material. According to Morel and Hering,<sup>[3]</sup> the dissolution rate of a solid material is proportional to its concentration gradient and can be expressed as

$$\frac{dC}{dt} = K(C_{\text{max}} - C_x) \quad (\text{S2})$$

where  $C_x$  is the concentration of the material in the bulk solution and  $C_{\text{max}}$  is the maximum equilibrium concentration. After making some assumptions (e.g.  $C_x = 0$  at  $t = 0$ ,  $C_{\text{max}} = C_{\text{Ag NPs}}$ ), Eqn S2 can have the general solution of:

$$\frac{C_x}{C_{\text{max}}} = 1 - e^{-kt} \quad (\text{S3})$$

Assuming the dissolution process would involve a fast process over a short period of time and a slower process over a longer time, Eqn S2 can be written as:

$$\frac{C_x}{C_{\text{max}}} = 1 - F_1 e^{-k_1 t} - F_2 e^{-k_2 t} \quad (\text{S4})$$

where  $F_1$  represents the fraction of a fast dissolution and  $F_2$  represents the fraction for slow dissolution. If we assume  $F_1 + F_2 = 1$ , then  $F_2 = 1 - F_1$ , and Eqn S4 can be rewritten as Eqn S5:

$$\frac{C_x}{C_{\text{max}}} = 1 - F_1 e^{-k_1 t} - (1 - F_1) e^{-k_2 t} \quad (\text{5})$$

The weighted square of fitting errors was calculated using Eqn S6:

$$X^2 = \sum \frac{(O - E)^2}{\sigma^2} \quad (\text{6})$$

where  $\sigma^2$  is the variance of the measured dissolved Ag fractions.

The fitting parameters ( $F_1$ ,  $k_1$  and  $k_2$ ) in this equation were optimised by *Solver* software in *Microsoft Excel* by minimising the weighted square error.

### Concentration dependent speciation of silver in seawater

Production of soluble silver chloro complexes  $[\text{AgCl}]^0$ ,  $[\text{AgCl}_2]^-$ ,  $[\text{AgCl}_3]^{2-}$ ,  $[\text{AgCl}_4]^{3-}$  and insoluble  $\text{AgCl}(s)$  depends on the  $\text{Ag}^+$  concentration.<sup>[4]</sup> The formation of silver chloro complexes and silver  $\text{AgCl}$  precipitates in seawater as a function of  $\text{Ag}$  ion concentrations (0.001 to 0.1 mM  $\text{Ag}$  with an increment of 0.001 mM  $\text{Ag}$ , or 0.1079–10.79 mg  $\text{L}^{-1}$ ) was calculated using *Visual MINTEQ* software version 3.0 (<http://www.lwr.kth.se/English/OurSoftware/vminteq>).

### References

- [1] M. Baalousha, A. Prasad, J. R. Lead, Quantitative measurement of the nanoparticle size and number concentration from liquid suspensions by atomic force microscopy. *Environ. Sci. Process. Impacts* **2014**, *16*, 1338. [doi:10.1039/c3em00712j](https://doi.org/10.1039/c3em00712j)
- [2] J. Zook, S. Long, D. Cleveland, C. Geronimo, R. MacCusprie, Measuring silver nanoparticle dissolution in complex biological and environmental matrices using UV–visible absorbance. *Anal. Bioanal. Chem.* **2011**, *401*, 1993. [doi:10.1007/s00216-011-5266-y](https://doi.org/10.1007/s00216-011-5266-y)
- [3] F. M. Morel, J. G. Hering, *Principles and Applications of Aquatic Chemistry* **1993** (Wiley: New York).
- [4] C. Levard, E. M. Hotze, G. V. Lowry, G. E. Brown, Environmental transformations of silver nanoparticles: impact on stability and toxicity. *Environ. Sci. Technol.* **2012**, *46*, 6900. [doi:10.1021/es2037405](https://doi.org/10.1021/es2037405)