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).[1] Suspension of citrate coated gold nanoparticles (cit-Au NPs) (1–20 µg 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 µg L⁻¹) in seawater was monitored systematically over a period of one month using a UV-Vis spectrophotometer (UV-2600, Shimatsu 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 Aliquots of 10 mL were withdrawn at different time intervals for UV-Vis measurement.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.[2]
The dissolved Ag fractions were calculated as:
\[
\text{Dissolved Ag fraction} = \frac{\text{UV}_{4000} - \text{UV}_{400t}}{\text{UV}_{4000}}
\]  
(S1)

where \( \text{UV}_{4000} \) 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,\(^3\) the dissolution rate of a solid material is proportional to its concentration gradient and can be expressed as
\[
\frac{dC}{dt} = K(C_{\text{max}} - C_x)
\]  
(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:
\[
\frac{C_x}{C_{\text{max}}} = 1 - e^{-kt}
\]  
(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:
\[
\frac{C_x}{C_{\text{max}}} = 1 - F_1 e^{-k_2t} - F_2 e^{-k_2t}
\]  
(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:
\[
\frac{C_x}{C_{\text{max}}} = 1 - F_1 e^{-k_2t} - (1 - F_1)e^{-k_2t}
\]  
(5)

The weighted square of fitting errors was calculated using Eqn S6:
\[
X^2 = \sum \frac{(0 - E)^2}{\sigma^2}
\]  
(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 AgCl(s) depends on the $\text{Ag}^+$ concentration. The formation of silver chloro complexes and silver 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 L$^{-1}$) was calculated using Visual MINTEQ software version 3.0 (http://www.lwr.kth.se/English/OurSoftware/vminteq).

**References**


