The Biological and Environmental Implications of Ag and TiO_2 Nanoparticles

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Introduction

The fate and transport of metal and metal oxide nanoparticles within environmental and biological systems is currently an area of focus within the scientific community due to both their unusual behavior relative to bulk materials and their entry into different ecosystems through use in various customer products. The study of their interactions with biologically and environmentally common organic molecules is of special interest as these are widely found in environmental systems as natural organic matter.

This research explores the aggregation and sedimentation of TiO_2 and Ag nanoparticles within aqueous environments at a range of pH values, ionic strengths, and particle concentrations resembling natural environments as a function of surface amino acid adsorption. Although the primary objective of this research lies in studying the fate and transport of Ag and TiO_2 nanoparticles when presented with amino acids such as L-cysteine, the formation of a charge-transfer complex between Ag nanoparticles and L-cysteine was observed and some insight was gained as to the complex structure, formation, and potential effects on the fate and transport of Ag NPs.

Methods

Stock solutions of 40 nm TiO_2 and 20 nm citrate-coated Ag nanoparticles were prepared by adding 1 mL TiO_2 (1000 mg/L) and 0.1 mL Ag (1000 mg/L) to 99 mL and 99.9 mL, respectively, of nanopure H_2O. This solution was then sonicated for 30 minutes. Stock solutions for each amino acid were prepared similarly. Each sample solution was prepared by adding 1 mL of the appropriate stock NP solution, 1 mL of the respective stock amino acid solution, and the appropriate volume of 1 M stock NaCl solution to a new 15 mL falcon tube rinsed with nanopure H_2O. The solution was then brought to a total volume of 10 mL and the pH adjusted using dilute (0.01 M) NaOH or HCl prepared in nanopure H_2O.

Analysis was performed using UV-Vis spectroscopy, dynamic light scattering and measurement of particle zeta potential. UV-Vis spectroscopy was performed using a 3 mL quartz cuvette with a 1 cm path length and calibrated with nanopure H_2O prior to measuring any samples. DLS and zeta potential measurements were performed using a Malvern Instruments Zetasizer and new 1 mL disposable plastic cuvettes.

Results

In all cases involving TiO_2 NPs, increasing IS led to increased aggregation and sedimentation of the nanoparticles.

Ag NPs in solution with L-alanine, L-glycine, L-DOPA (oxidized), L-DOPA (reduced) and L-glycine also all exhibited an increase in aggregation and particle size, as measured by DLS, in addition to decreases in absorption values at a wavelength of 396 nm indicating increased aggregation relative to Ag NP control samples.

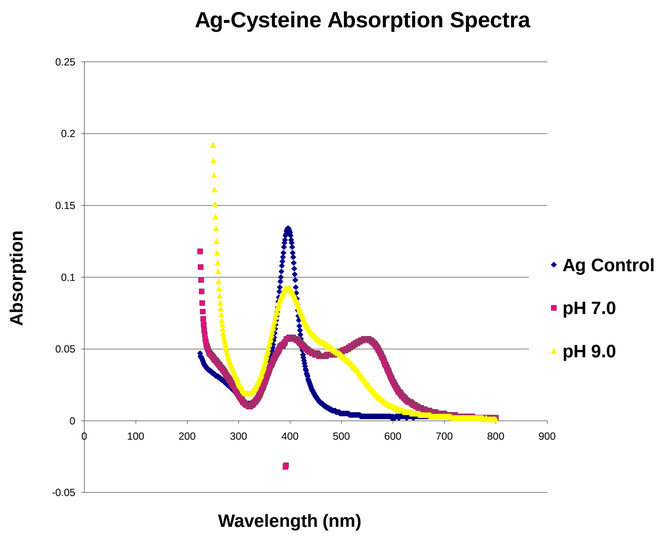

Figure 1 Red-shift in absorption wavelength maximum shown to be proportional to Ag NP aggregation in suspension.

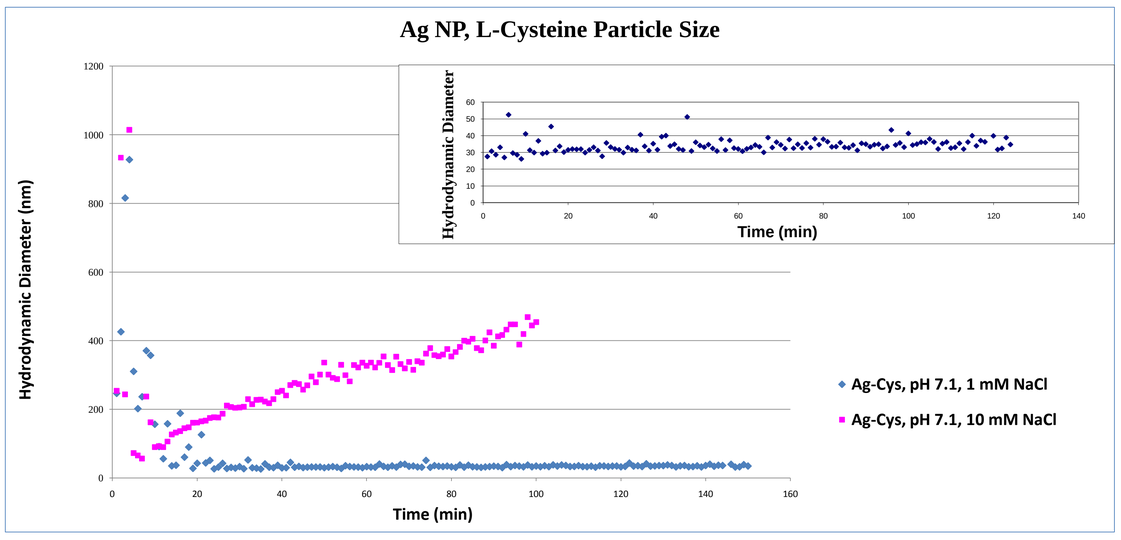

Figure 2 DLS data indicates that brief period of NP instability results in particle size of approximately 30 nm. The IS of the solution then determines the degree of aggregation of the Ag-cysteine complex.

The behavior of Ag NPs in solution with L-cysteine was measured over a wide range of IS, pH values and in seawater containing natural organic matter (NOM) (Figure 3). As shown in Figure 2, the DLS data for these samples indicates a brief period of NP instability resulting in the presence of particles approximately 30 nm in diameter. In solutions containing concentrations of NaCl greater than 1 mM the particles aggregate relatively quickly, reaching a diameter of approximately 450 nm in solutions containing 10 mM NaCl over 100 minutes. Solutions containing 1 mM NaCl experience very little aggregation and maintain stability at approximately 35 nm over a period of 100 minutes. In seawater solutions, the Ag NPs demonstrated a marked increase in particle size when in the presence of L-cysteine relative to Ag NP controls.

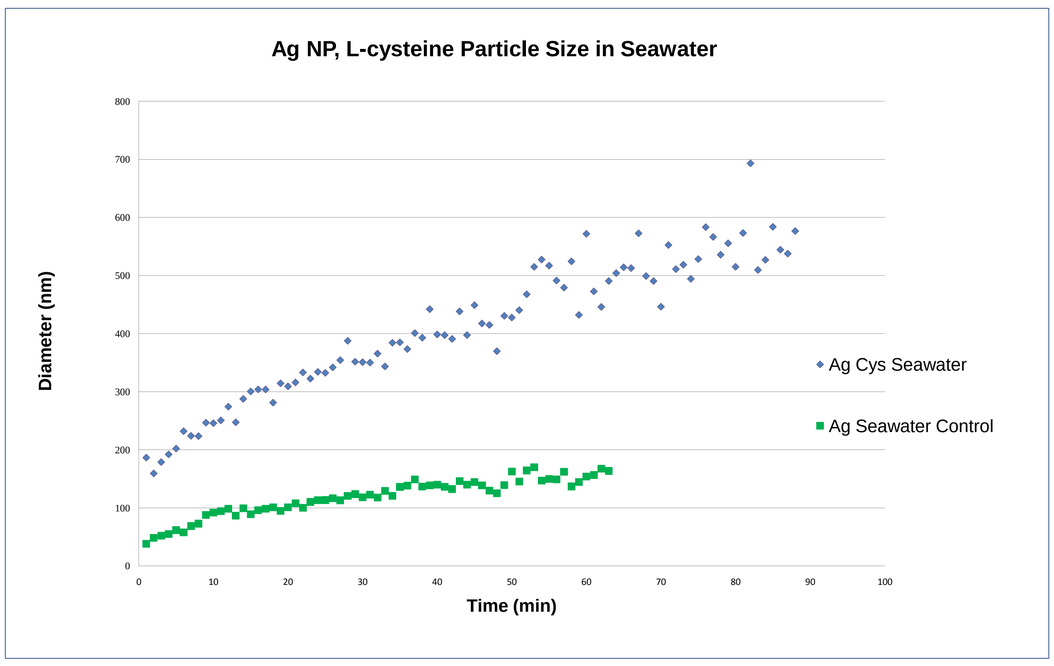

Figure 3 DLS data measuring the size of Ag NPs in seawater samples. Both samples contain1 mg/L Ag NP.

Conclusions

The formation of the Ag-cysteine complex is seen to be highly dependent on both the pH value and IS within the solution. The stability of this complex in suspension is primarily dependent on IS, resulting in stabilization at approximately 35 nm diameter in suspensions containing 1 mM NaCl or accelerated aggregation of particles in solutions of higher IS. The complex formation appears to be dependent on coadsorption of chloride ions with L-cysteine on the surface of the Ag NPs, allowing for the positively charged amino group of L-cysteine to interact with the positively charged Ag NP surface.

Although it is clear that the formation of the Ag-cysteine complex is able to stabilize Ag NPs in some cases, it appears to have the opposite effect in solutions containing a high IS. This is likely a result of the L-cysteine molecules outcompeting the NOM present in the natural seawater in adsorption to the NPs. NOM, however, either adsorbs significantly more weakly to the Ag-cysteine complex or is not able to adsorb at all, preventing steric stabilization and resulting in the increased aggregation of the particles.

These findings are significant in that they demonstrate the ability of Ag NPs, an increasingly commonplace addition to consumer products, are able to be stabilized in specific aqueous environments using environmentally and biologically prevalent molecules. The stabilization of these particles increases the likelihood that the nanoparticles will remain able to interact with other molecules or be taken up into biological systems.

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