Ligand-Dependent Ag\textsubscript{2}S Formation: Changes in Deposition of Silver Nanoparticles with Sulfidation

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Environmental Significance

The environmental transformation of sulfidation has been recognized to impact nanoparticle (NP) behavior. Some recent studies have led to the generalization that, during sulfidation, original ligands will be removed, and Ag$_2$S will become the new ligand shell. For the first time, this study demonstrates that the formation of Ag$_2$S is ligand-dependent and significantly impacts the consequent mobility and risk of the transformed AgNPs. Due to the selective formation of Ag$_2$S, not all sulfidized NPs have the same mobilization potential, and therefore it is important to characterize the continuous evolution of specific NP surfaces for better prediction of NP exposure and toxicity.
Ligand-Dependent Ag₂S Formation:
Changes in Deposition of Silver Nanoparticles with Sulfidation

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The surfaces of nanoparticles (NPs) are continuously evolving as they are exposed to different environmental conditions. Under the same sulfidation condition, silver NPs (AgNPs) are generally considered to undergo the same surface modifications (i.e., removal of original ligands and formation of a new silver sulfide (Ag$_2$S) shell). We examined this generalization by studying how different ligands, polyvinylpyrrolidone (PVP) and thiolated polyethylene glycol (PEG), affected 1) the formation of a new Ag$_2$S shell and 2) the subsequent mobility of these transformed AgNPs. The deposition of PEG-AgNPs onto a silica substrate decreased by a factor of 40 after sulfidation while the deposition of PVP-AgNPs increased by a factor of 15. The decreased deposition of sulfidized PEG-AgNPs was attributed to the removal of PEG and the formation of Ag$_2$S, which created a more negatively charged surface (-15 mV to -30 mV) and consequently greater electrostatic repulsion with the silica substrate. The increased deposition of sulfidized PVP-AgNPs was suggested to be caused by the removal of PVP and absence of Ag$_2$S, which decreased steric repulsion with the silica substrate. For the first time, this study revealed the unique abilities of two common polymeric coatings of AgNPs to form Ag$_2$S during sulfidation and how that Ag$_2$S determined their subsequent mobility. The results of this communication also highlighted the importance of monitoring the continuous evolution of the NP surface for better prediction of NP exposure and toxicity.
Introduction

The surfaces of environmental nanoparticles (NPs) are continuously evolving along with changes in its environment (e.g., pH, ionic strength, natural organic matter). Environmental transformations (e.g., dissolution\textsuperscript{1–9} and sulfidation\textsuperscript{10–13}) have been shown to significantly impact the stability and toxicity of NPs. As NPs move through different aquatic environments, they are exposed daily to different redox conditions and constituents in the environment (e.g., UV irradiation\textsuperscript{14–16} and natural organic matter\textsuperscript{16}). These exposures can result in changes in the composition (and/or steric arrangements) of the “pristine” macromolecules functionalized on the surfaces of NPs. Since the impact of macromolecular coatings and transformation processes were both recently reviewed and discussed at length elsewhere,\textsuperscript{17,18} it is not the intent of this introduction to provide a comprehensive overview of these topics but instead to briefly highlight a subset of the literature that is most relevant to this study.

Two pertinent studies by Louie et al.\textsuperscript{14,19} demonstrated that NP aggregation could be caused by photo-induced transformation of polyvinylpyrrolidone (PVP) and thiolated polyethylene glycol (PEG) coated on gold NPs. These two polymers underwent fundamentally different transformations. While collapsed PVP was found to persist on gold NPs after UV irradiation, the methoxy PEG thiol coating was truncated through a chain scission mechanism.\textsuperscript{14,19} In addition to highlighting the importance of characterizing ligand transformation for better prediction of NP fate and transport, they also stated that the transformation of polymeric NPs 1) cannot be generalized across different coating types and 2) cannot be assessed using unbound polymers.

Partial sulfidation of AgNPs was observed to be highly prevalent in wastewater treatment.\textsuperscript{20} Since sulfide phases are typically much less soluble, sulfidation has been proposed as a natural detoxification mechanism for metal NPs.\textsuperscript{11,12} A common misconception is that metal sulfides are relatively immobile because of their low solubility; however, the reactivity of metal sulfides changes at the nanoscale. Despite the low solubility products of silver sulfide (Ag\textsubscript{2}S) (K_{sp} = 6.00 x 10\textsuperscript{-51}), large extents of Ag\textsubscript{2}S NP dissolution have been reported.\textsuperscript{21} In addition to the intrinsic toxicity of the metals, metal sulfides are also capable of scavenging other contaminants.\textsuperscript{22–27}

Overall, findings from recent AgNP sulfidation studies\textsuperscript{11,28,29} generally consider that, during sulfidation, original “pristine” ligands will be removed/modified and Ag\textsubscript{2}S will emerge as the new ligand shell. This communication examines that generalization by asking the question:
would Ag₂S form on the surface of AgNPs regardless of ligand type? In other words, this study sets itself apart by focusing on one important but not well-studied consideration: how different pristine ligands influence 1) the formation of a new Ag₂S ligand shell and 2) the subsequent deposition of AgNPs on environmental surfaces.

**Results and Discussion**

**Sulfidation Alters AgNP Mobility**

The deposition of AgNPs (before and after transformation) onto silica substrate was studied through quartz crystal microgravimetry (QCM) and suggested that sulfidation alters AgNP mobility. The mobility of PEG-AgNPs increased after sulfidation as demonstrated by a 40-fold decrease in deposition (Fig. 1A). In contrast, the mobility of PVP-AgNPs decreased after sulfidation as demonstrated by a 15-fold increase in deposition. The trends of increased and decreased mobility for PEG-AgNPs and PVP-AgNPs, respectively, were observed in the absence (Fig. 1A) and presence of natural organic matter (NOM) at different pH conditions (Fig. S1). The deposition behavior of PEG-AgNPs and PVP-AgNPs suggested that the polymeric coating of AgNPs is crucial in determining their subsequent mobility in a sulfidizing environment.

The zeta potentials of pre- and post-sulfidized PEG-AgNPs and PVP-AgNPs were determined to evaluate the role of electrostatic forces in the observed changes in deposition. Zeta potentials of PEG-AgNPs (Fig. 1B) showed a decrease from -15 mV to -30 mV due to sulfidation. The more negative zeta potentials suggested that 1) the decrease in deposition was likely due to greater electrostatic repulsion between the negatively charged silica substrate and the negatively charged PEG-AgNPs, and 2) sulfidation promoted surface modification of the AgNPs. In contrast, the zeta potential values of PVP-AgNPs (Fig. 1B) showed no significant (p>0.05) changes after sulfidation. The similar zeta potentials of PVP-AgNPs before and after sulfidation suggested that 1) the change in PVP-AgNP deposition was not due to changes in electrostatic interactions with the silica substrate, and 2) PVP-AgNPs and PEG-AgNPs responded differently to sulfidation, as discussed below.

**Removal of PEG and Ag₂S Formation**

The chemical transformations of PEG-AgNPs and PVP-AgNPs were investigated through attenuated total reflection-Fourier transform infrared (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS). The ATR-FTIR spectra of pristine PEG-AgNPs (Fig. 2A) showed three
distinct bands at 1105 (C-O stretching), 1353 (C-H bending), and 2875 (C-H stretching) cm\(^{-1}\) and were consistent with the literature.\(^{30}\) After sulfidation, the three major peaks disappeared completely from the ATR-FTIR spectra, which suggested that PEG was removed during sulfidation. The removal of PEG is further supported by the atomic C % before and after sulfidation (Table S1). After sulfidation, the atomic C % decreased from \(~64\%\) to \(~19\%\).

The Ag\(_{3d5/2}\) and Ag\(_{3d3/2}\) XPS spectra were studied to examine changes in the surface Ag composition. In the pristine state, PEG-AgNPs (Fig. 3A) had binding energies of \(~367\ eV\) and \(~373\ eV\), which were attributed to a combination of silver oxide (Ag\(_2\)O), silver carbonate (Ag\(_2\)CO\(_3\)), and elemental silver and are consistent with previously reported values.\(^{31,32}\) After sulfidation, there was a clear shift in the binding energies from \(~367\) to \(~368.2\ eV\) and from \(~373\) to \(~374.2\ eV\) (Fig. 3A). The binding energies of \(~368.2\ eV\) and \(~374.2\ eV\) in the sulfidized PEG-AgNPs were attributed to silver sulfide and were consistent with XPS analysis of Ag\(_2\)S particles (Fig. S2). The formation of silver sulfides on PEG-AgNPs supported our complementary characterizations. As the PEG was removed, the AgNP surface was likely exposed to sulfide which allowed for the formation of silver sulfides. The zeta potentials of sulfidized AgNPs were consistent with Ag\(_2\)S (\(-21\) to \(-30\) mV). The more negative zeta potential of the sulfidized PEG-AgNPs likely increased the electrostatic repulsion forces between the NPs and silica substrate and resulted in the observed decrease in deposition.

**Removal of PVP and the Absence of Ag\(_2\)S Formation**

The ATR-FTIR spectra of pristine PVP-AgNPs (Fig. 2B) showed four distinct bands at 1289 (C-N stretching), 1424 (C-H bending), 1661 (C=O stretching), and 2954 (C-H stretching) cm\(^{-1}\) and were consistent with the literature.\(^{33}\) After sulfidation, the four major peaks remained present but at lower intensities, which suggested some removal of PVP during sulfidation. The removal of PVP was further supported by the atomic C and N % of PVP-AgNPs (Table S1). After sulfidation, the atomic C % decreased from \(~71\%\) to \(~33\%\) and the atomic N % decreased from \(~11\%\) to \(~2\%\).

The Ag\(_{3d5/2}\) and Ag\(_{3d3/2}\) XPS spectra of pristine PVP-AgNPs (Fig. 3B) showed that PVP-AgNPs had binding energies similar to those of pristine PEG-AgNPs. The binding energies of 367.4 eV and 373.4 eV were attributed to silver oxide and silver carbonate. In contrast to PEG-AgNPs, there were no observable shifts in binding energies after sulfidation for PVP-AgNPs (Fig. 3B).
The unchanged binding energies suggested that the removal of PVP did not promote the formation of silver sulfide which was observed for PEG. The removal of PVP and the absence of a Ag$_2$S shell likely reduced the steric forces between the PVP-AgNPs and silica substrate and promoted deposition.

The formation of a new Ag$_2$S shell appeared to be dependent on the residual ligand coating. A decrease in atomic C % (Table S1) suggested that both ligands were removed during sulfidation, but the ATR-FTIR spectra (Fig. 2AB) suggested that the extent of removal was ligand-dependent. The ATR-FTIR bands of PEG-AgNPs (Fig. 2A) disappeared while the bands of PVP-AgNPs (Fig. 2B) remained at lower intensities after sulfidation which suggested that more PEG may have been removed relative to PVP. The greater removal of PEG (i.e. lower degree of residual PEG coating; Table S1) likely exposed more of the AgNP surface to sulfide, which promoted the formation of silver sulfides. The remaining bound PVP likely inhibited the exposure of the Ag surface to sulfide and consequently prevented the formation of a Ag$_2$S shell.

One possibility for the difference in the degree of ligand removal may be modification of the PVP due to sulfidation. As observed previously, environmental transformation (UV irradiation) can result in the truncation of ligands through a scission mechanism.$^{19}$ In addition, a study by Zhou et al.$^{34}$ reported the energetic preference for PVP to bind to Ag $\{100\}$ facets to be twice that of PEG. For our system, further characterizations are needed to distinguish between the modification and the desorption of the PVP ligand; we hypothesize that it is likely to be a combination of both that contribute to the loss of ligand.

This communication for the first time revealed the unique importance of two common polymeric coatings of AgNPs, PVP and thiolated PEG, regarding their different ability to form Ag$_2$S during sulfidation and how that becomes crucial in determining their subsequent mobility. We found that Ag$_2$S formation is ligand-dependent and essential for the persistence of AgNPs after sulfidation. Under our experimental conditions, sulfidation enhanced the immobilization of PVP-AgNPs, therefore decreasing the chances of exposure. For PEG-AgNPs, sulfidation promoted NP mobilization but decreased toxicity due to the formation of Ag$_2$S.

Rational optimization of NP surfaces for specific applications essentially relies on a detailed mechanistic understanding of NP-ligand interactions. Our findings could better inform material chemists as they design and select polymers for stabilization/functionalization of nanomaterials.
Future work can focus on studying the deposition of NPs under a variety of environmentally relevant conditions (e.g., heterogeneous collector surfaces). The results of this work also highlight the importance of monitoring the continuous evolution of NP surface for better prediction of NP toxicity and exposure.

**Materials and Methods**

**Preparation of AgNPs**

Spherical PEG- and PVP-capped AgNPs (NanoComposix, San Diego, CA; TEM diameter: 50 nm) were used without further purification. The molecular weights of the PEG and PVP capping agents were 5 kDa and 40 kDa, respectively. The NP stock solutions were diluted from 5000 mg/L (PEG-AgNPs) and 1000 mg/L (PVP-AgNPs) to 100 mg/L with ultrapure deionized water (Milli-Q™, 18.2 mΩ) to obtain a final particle concentration of $1.24 \times 10^{10}$ particles/L. Filtered (0.20 µm) stock solutions of NaNO$_3$ and HEPES were used to adjust the final electrolyte concentration to 50 mM NaNO$_3$ and 1 mM HEPES. The final pH of the suspensions was adjusted to 5.0 ± 0.2 and 7.0 ± 0.2.

Unfractionated Suwanee River NOM (International Humic Substances Society) was dissolved in ultrapure deionized water and filtered (0.20 µm). The organic carbon content of the NOM stock solution was determined through total organic carbon analysis (Shimadzu TOCV; Kyoto, Japan). All stock suspensions and solutions were stored in the dark at 4°C.

The sulfidation of AgNPs was conducted using sodium sulfide (Na$_2$S) in the manner described by Levard et al. (2011). The AgNP suspensions were mixed with Na$_2$S in the presence of 40 mg/L NOM to obtain a S/Ag ratio of 1.079. The suspensions were mixed in the dark for 24 hr. After 24 hr, the suspensions were centrifuged at 3700 G for 25 min, and the supernatant was decanted. The NP suspensions were washed at least two times with ultrapure deionized water to remove excess sulfide and NOM. After the final washing step, ultrapure deionized water was added to the suspension to reach the desired particle concentration. The pristine and sulfidized NPs are suspended in the same solution chemistry for all experiments and characterizations.

**Deposition of AgNPs**

The real-time deposition of pristine and sulfidized AgNPs onto silica substrate (QSX 303, Q-Sense AB, Gothenburg, Sweden) were monitored and quantified through QCM. The deposition extent, in ng/cm$^2$, was determined by measuring oscillation frequency changes in the quartz
crystal (due to NP deposition) and relating those changes to mass changes through the Sauerbrey relationship. The deposition experiments were conducted in the same solution chemistry as described above, at 25 ± 0.2 °C, and in the absence and presence of NOM (5 mg/L). The deposition experiments were repeated at least three times; the average values and standard deviations (error bars) are reported.

**Characterization of AgNPs**

The electrophoretic mobility of the pristine and sulfidized AgNPs were measured at 25 ± 0.2 °C using a Malvern Zetasizer NS (Worcestershire, UK). The zeta potential value was derived from the electrophoretic mobility using the Smoluchowski equation. In addition to the pristine and sulfidized AgNPs, the zeta potential of Ag₂S (Sigma-Aldrich) was measured. The Ag₂S particles were ground by mortar and pestle, suspended in ultrapure deionized water at the solution chemistry described above, and filtered (0.45 µm) prior to measurement. All reported values represented the average of at least three replicates and included a minimum of thirteen runs.

The ATR-FTIR analysis was conducted on pre- and post-sulfidized NP samples to characterize changes in ligand-NP interactions. All ATR-FTIR spectra were collected using a Perkin-Elmer Spectrum One FTIR spectrometer, equipped with a lithium tantalate (LiTaO₃) detector and a one-reflection horizontal ATR accessory with a diamond/ZnSe crystal (Shelton, CT). Approximately 30 µL of sample were drop-casted onto the crystal and air dried prior to spectra collection. Atmospheric background spectra were subtracted from the samples and baseline correction was completed through the Spectrum software. All spectra were obtained by collecting 250 scans with a spectral resolution of 4 cm⁻¹ between 650 and 4000 cm⁻¹ at a scan speed of 1.0 cm/s. Measurements were replicated at least two times.

The XPS analysis was used to examine changes in the AgNP surface chemistry before and after sulfidation. Prior to XPS analysis, samples were deposited onto a glass slide and air-dried. Spectra were collected on a Physical Electronics Quantum 2000 Scanning ESCA Microprobe, and analyzed using PHI’s software based on MATLAB, MultiPak v.9.0. An internal metal standard (i.e. Ag) was used for the standardization of the spectra. Specifically, the peak at 368.3 eV for the Ag₂S (Sigma-Aldrich) was used to determine if shifts in the sample spectra were needed.

**Conflicts of Interest**
There are no conflicts to declare.

Acknowledgments

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Supplementary Information

The Supplementary Information includes the deposition data of pristine and sulfidized PEG- and PVP-AgNPs in the presence of NOM, the atomic C and N % of pristine and sulfidized PEG- and PVP-AgNPs, and the Ag\textsubscript{3d5/2} and Ag\textsubscript{3d3/2} XPS spectra of Ag\textsubscript{2}S.

References


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Figure 1. The (A) deposition and (B) zeta potential of pristine and sulfidized PVP- and PEG-capped AgNPs onto QCM silica sensors in 5 mM NaNO₃ (pH 7). Error bars represent the standard deviation of at least three replicate experiments.
Figure 2. The ATR-FTIR spectra of (A) PEG- and (B) PVP-capped AgNPs in the pristine and sulfidized states.
Figure 3. The Ag$_{3d5/2}$ and Ag$_{3d3/2}$ XPS spectra of (A) PEG- and (B) PVP-coated AgNPs in the pristine and sulfidized states.
The formation of silver sulfide on the surface of silver nanoparticles is ligand-dependent and is essential for their persistence after sulfidation.