



Stability of silver nanoparticle sulfidation products

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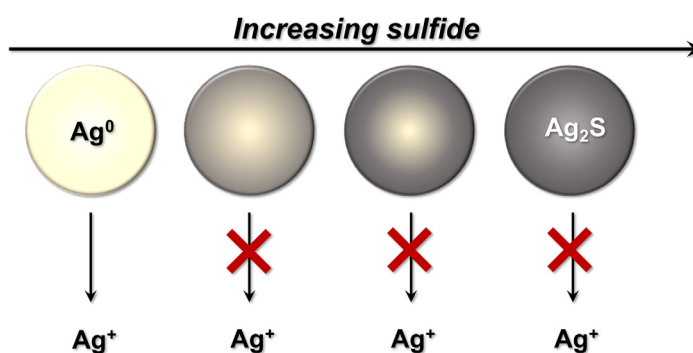
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HIGHLIGHTS

- Silver nanoparticle sulfidation product stability was measured over two months.
- Sulfidized silver nanoparticles were analyzed for acid volatile sulfide.
- Excess sulfide allowed silver sulfide with bulk Ag_2S stoichiometry to form.
- Even partial sulfidation prevents silver ion release from nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

The adoption of silver nanoparticles in consumer goods has raised concerns about the potential environmental harm of their widespread use. We studied chemical transformations that Ag NPs may undergo as they pass through sulfide-rich conditions common in waste water treatment plants (WWTPs), which may limit the release of Ag^+ from Ag NPs due to the formation of low-solubility silver sulfide (Ag_2S). However, it is uncertain whether sulfidation is complete and if sulfidized Ag NPs continue to release Ag^+ . To address these uncertainties, we monitored the reaction of Ag NPs with various levels of sulfide with an ion selective electrode and UV/visible spectrophotometry over the course of two months. We characterized the products of the sulfidation reactions with a purge-and-trap acid volatile sulfide (AVS) analysis, which served as a measure of the stability of the sulfidized products because sulfide would be readily lost to oxidation unless it is stabilized as Ag_2S . The Ag NP surface plasmon resonance (SPR) absorbance peak was initially diminished and then returned over the course of several days after reaction with limited amounts of sulfide, suggesting a dynamic system that may retain some characteristics of the pristine Ag NPs. However, ICP-MS analysis of sulfidized Ag NP suspensions over a two-month period demonstrates that sulfidation limits the release of Ag^+ ions from nanosilver that pass through a WWTP, even when sulfide concentrations are limited relative to silver.

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1. Introduction

Today over 3000 consumer products contain nanoparticles (Council, 2018). As nanotechnology becomes increasingly prevalent in daily life, concerns have been raised about the environmental implications of

widespread use of nanomaterials (Nowack and Bucheli, 2007). Of the nanomaterials now commonly found in consumer products, many contain metals that can be detrimental environmental effects (Peng et al., 2017). Silver nanoparticles (Ag NPs) are currently one of the most widely used types of nanoparticle due to their anti-microbial properties (Yu et al., 2013) and are known to readily leach out of many consumer products (Benn and Westerhoff, 2008; Hedberg et al., 2014). If Ag NPs reach aquatic ecosystems, they have potentially toxic effects, either

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due to the oxidative release of silver ions (Fabrega et al., 2011; Liu and Hurt, 2010), or the toxicity of Ag NPs themselves (Ivask et al., 2014).

However, Ag NPs released from consumer goods are expected to encounter a wastewater treatment plant (WWTPs) before reaching natural waters (Levard et al., 2012). Therefore anticipating the environmental implications of nanosilver requires an investigation of Ag NP chemistry in conditions representative of WWTPs. The anaerobic conditions in WWTPs have been shown to promote the sulfidation of Ag NPs to produce silver sulfide (Ag₂S) (Kent et al., 2014; Liu et al., 2011), and Ag₂S nanoparticles have been identified in sewage sludge (Kim et al., 2010). The complete reaction of Ag NPs with sulfide requires an oxidant (e.g., oxygen) for the Ag NPs (with an oxidation state of 0) to become Ag (I) in Ag₂S, as shown in reaction 1:



The low solubility of Ag₂S (Liu et al., 2010) mitigates the toxicity of Ag⁺ by limiting its bioavailability (Bianchini et al., 2002) so an understanding of Ag NP sulfidation is imperative to assess the ecotoxicity of Ag NPs. Although this could indicate a chemical sink for Ag NPs introduced to the water system, the application of sewage sludge to agricultural fields could be a pathway for reintroduction of silver to the environment (Pradas Del Real et al., 2016).

To date most studies investigating the environmental implications of Ag NP use have studied the reactions and toxicity of Ag NPs in a pristine state (Wiesner et al., 2011), similar to what would be found in consumer products. These studies have investigated how Ag NPs are subject to oxidation (Baalousha, 2009; Liu and Hurt, 2010; Peretyazhko et al., 2014), aggregation (Baalousha et al., 2013; El Badawy et al., 2012) and changes to surface chemistry (Gondikas et al., 2012; Kanel et al., 2015) in conditions representative of natural waters. Similarly, most sulfidation studies have focused on the initial chemical transformations “virgin” Ag NPs may undergo upon reaction with sulfide (Liu et al., 2011; Thalmann et al., 2016; Zhang et al., 2016) and studies investigating the stability of the resulting sulfidized products likely to form in WWTP are more limited (Levard et al., 2011). Because of the profound chemical and physical changes that can occur when nanomaterials are introduced to WWTP conditions (Kent et al., 2014; Kim et al., 2010), it is imperative that the stability of these transformed materials are examined in addition to pristine, unreacted nanomaterials.

The main goal of this study is to better understand how sulfidation of Ag NP can act as a control on the dispersal of silver in the environment from Ag NPs in consumer goods. Although we have used an idealized system without many of the complexities present in a true WWTP, it is a necessary first step in understanding the most basic interactions between Ag NPs and sulfide before the role of other chemical parameters (e.g., organic material) in Ag NP sulfidation can be addressed. This study includes the first application of acid volatile sulfide (AVS) to assess the stability of sulfide within any Ag₂S that forms as a result of Ag NP sulfidation. Dissolved “free” sulfide (H₂S or HS⁻) and even some metal sulfides are susceptible to oxidation of sulfide to other sulfur species (e.g., polysulfides, sulfite, sulfate) (Rickard and Luther, 2006). We also use UV/vis measurements of the surface plasmon resonance of Ag NPs to detect any changes to the Ag NP surfaces, including dilution studies in a long pathlength cell to assess the role of overall Ag NP concentration in the stability of sulfidation products. Finally, inductively coupled plasma mass spectrometry (ICP-MS) was used to monitor the concentration of dissolved silver released from Ag NP sulfidation products over a two-month period.

2. Materials and methods

2.1. Materials

Distilled or deionized (18.2 MΩ·cm or greater resistivity) water was used for all solution preparation and experiments. All chemical reagents

used were ACS grade or higher and were used as received. Silver nanoparticle stock solutions and silver standards were prepared from silver nitrate (AgNO₃, ACS grade, BDH). Adjustments to pH were made using 1 M or 0.1 M aqueous solutions of HCl (Fisher certified ACS Plus), HNO₃ (69%, Veritas redistilled), or NaOH (ACS grade, BDH). The anti-oxidant buffer was prepared using EDTA (USP/FCC, Fisher), NaOH, and ascorbic acid (ACS grade, MACRON). Measurements of pH were made with a Mettler Toledo InLab Expert pro pH electrode with a Mettler Toledo Seven Excellence Meter, which was calibrated daily with pH 4.00, 7.00 and 10.00 buffers as needed.

2.2. Silver nanoparticle synthesis and purification

The Ag NP synthesis was carried out by reducing AgNO₃ with NaBH₄ (99% Venpure ACROS) in the presence of sodium citrate (ACS grade, BDH), which acted as a capping agent. An excess of freshly prepared aqueous NaBH₄ solution was added dropwise to a 500-mL solution of 200 μM AgNO₃ and 600 μM citrate. The solution immediately turned gray, then yellow, indicating the formation of Ag NPs. Following 30 min of stirring, Ag NPs were separated from large particles and aggregates and small excess reagents by syringe filtering (0.22-μm pore size) and ultrafiltration (3 kDa), respectively. The ultrafiltration membranes were pre-conditioned using water in a stirred cell under 280 kPa pressure of ultra-high purity (UHP) N₂ gas. The Ag NP solution was syringe filtered directly into the ultrafiltration chamber and ultrafiltered under a pressure of 40 psi nitrogen at a flow rate of about 2 mL per minute. Citrate (0.35 mM) was added (100 mL) as a washing solution once the solution volume was reduced to about 20% of its original volume. This was repeated twice more and ultrafiltration continued until the Ag NP stock solution was concentrated to ~10% of its original volume (50 mL as described). The Ag NP stock solution was stored in the dark at 4 °C to maintain stability (Gorham et al., 2014). The total concentration of silver in the stock solution was determined by flame atomic absorbance spectroscopy (FAAS, described below) and the stability of the stock was ensured by regular monitoring of the surface plasmon resonance peak characteristic of Ag NPs at about 400 nm (UV/vis, described below). The characterization of similarly prepared citrate-capped Ag NPs has been previously reported and indicated Ag NPs with approximate diameters of 5–10 nm (Fig. S1 and Mullaugh and Pearce, 2017).

2.3. Preparation of sulfidized Ag NPs

A sulfide stock solution was prepared by dissolving sodium sulfide in distilled water that had been purged with UHP N₂ gas for at least 30 min to prevent the oxidation of sulfide by dissolved oxygen in stock solutions. Varying amounts of sulfide were added to unpurged Ag NP solutions containing 32 μM silver for sulfide concentrations ranging from 2 to 64 μM sulfide, plus controls containing no sulfide. Samples were stored at room temperature in loosely capped brown Nalgene bottles to ensure saturation of the solution by oxygen while minimizing the influence of light and evaporation. Solutions were analyzed immediately to monitor the loss of free sulfide over time. Only when sulfide was in a large excess to silver (64 μM sulfide) was free sulfide detected in the solution after one day. Long term changes in the solutions were monitored over the course of several weeks for acid volatile sulfide, total silver by FAAS, and the surface plasma resonance band of Ag NPs by UV/vis.

2.4. Acid volatile sulfide analysis

The acid volatile sulfide (AVS) measurements from Ag NP sulfidation products were performed using a purge-and-trap method (Bowles et al., 2003) in which Ag₂S is acidified to generate H₂S gas that is removed from the sample with a carrier gas (UHP N₂) and recovered in

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