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# Is there a silver lining? Aggregation and photo-transformation of silver nanoparticles in environmental waters

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The nanotechnology industry advances rapidly, and at the vanguard are the promising silver nanoparticles (AgNPs), which have diverse applications. These nanometer-sized particles have been shown to inhibit the ability of bacteria to produce adenosine triphosphate (ATP), a molecule necessary for chemical energy transport in cells. The antimicrobial properties of AgNPs (and Ag<sup>+</sup>) make them valued antibacterial agents (Maramba-Jones and Hoek, 2010; Ahamed et al., 2010; Seil and Webster, 2012; Xiu et al., 2012; Chernousova and Epple, 2013). As a result, AgNPs are used in the sterilization of medical instruments and as wound gauze (Fig. 1a). The disinfectant properties of AgNPs have also facilitated their use as liners in household appliances and personal clothing.

However, greater applications of AgNPs carry the challenge of handling greater wastes. AgNPs are not always stable within consumer products (Benn and Westerhoff, 2008; Pasricha et al., 2012). For example, if a wound dressing containing AgNPs is soaked in water, the AgNPs can be released from the wound dressing (Fig. 1) (Holbrook et al., 2014). Disposal of consumer products that contain AgNPs could result in contamination of the environment, notably the aquatic environment (Tolaymat et al. 2010; Gottschalk and Nowack 2011; Fabregaa et al., 2011).

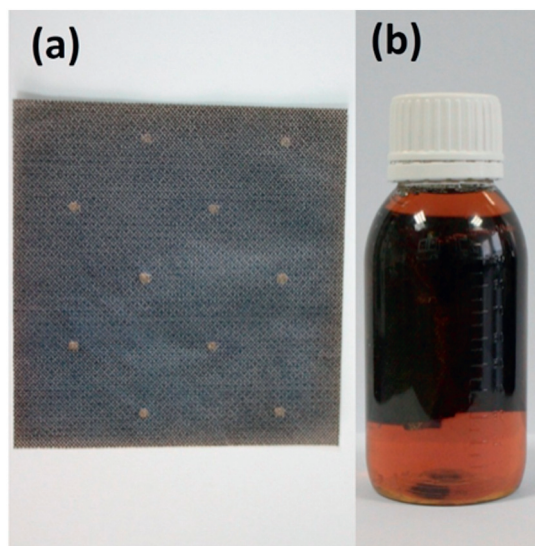
The toxicity of AgNPs depends on their size, shape, surface properties, and the chemical speciation of their transformation products (e.g., silver ions) (Hussain et al., 2005; AshaRani et al., 2009; Wijnhoven et al., 2009; Johnston et al., 2010; Qian et al., 2013; Pratsinis et al., 2013; Burkowska-But et al., 2014; Kuppusamy et al., 2015). While a nanoparticle can be defined as having a diameter in the range of 1 to 100 nm, smaller AgNPs, such as those with 5.5 nm diameter, are less stable and are 50-fold more dissolvable in water than larger AgNPs (diameter 76.6 nm) (Ma et al., 2012). Methods to stabilize the shape of AgNPs and prevent their dissolution include coating them with a polymer, such as polyvinylpyrrolidone (PVP), or treating them with sodium citrate.

Nanoparticles can undergo aggregation to form larger nanoparticles. Aggregation of AgNPs has been shown to decrease their toxicity to aquatic organisms, such as bacteria and protozoans (Kvitek et al., 2008; Juganson et al., 2013). Multiple studies (El Badawy et al., 2010, 2012; Huynh and Chen, 2011; Li and Lenhart, 2012) have shown aggregation of AgNPs as an important process in the aquatic environment. What environmental water parameters govern the aggregation of AgNPs and how do they behave in different natural water bodies?

Yin et al. (2015) at the State Key Laboratory of Environmental Chemistry and Ecotoxicology, Chinese Academy of Sciences, addressed this issue in their study recently published in the *Journal of Environmental Sciences*. They examined the fate and interactions of AgNPs in seven natural water bodies near Beijing. These local natural water bodies include three rivers (Chaobai, Wenyu, and Yongding), two lakes (Fuhai and Gaobeidian), a canal (Jingmi), and a spring (Fenghuangling), representing environmental water samples of different ionic strength, hardness, and dissolved organic matter (DOM). While keeping the initial composition, coating, and size of AgNPs controlled, Yin et al. (2015) simulated the “disposal” of AgNPs

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**Fig. 1 – The release of AgNPs from a consumer product, wound dressing. (a) AgNP-containing wound dressing; (b) the wound dressing placed in a jar containing water. The yellow color in the jar represents AgNPs released from the wound dressing. Photo courtesy of Dr. Yongguang Yin, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing.**

into these waters. Their study highlights the importance of water chemistry in the aggregation and stability of AgNPs.

Yin et al. (2015) first synthesized AgNPs and coated the AgNPs with PVP because PVP is a commonly used stabilizer for AgNPs. They injected these AgNPs into their water samples at mg/L concentrations. They then examined how the various water chemistry conditions impacted the aggregation of AgNPs. Their water samples varied in ionic strength, hardness, and DOM content. To characterize the aggregation of AgNPs, they used three analytical techniques: UV-visible absorption spectroscopy, dynamic light scattering (DLS), and Raman spectroscopy. The UV-visible absorption spectroscopy measured changes in the characteristic absorbance of AgNPs, at a maximum wavelength of 402 nm, as the AgNPs aggregated. The DLS technique provided the information on the changes in the hydrodynamic radius of AgNPs. Raman spectroscopy was able to detect changes of the PVP-coated surface of AgNPs in contact with the constituents in the natural water samples. Using these techniques, the authors observed various degrees of aggregation in all natural water samples in comparison to deionized water. They found that water containing higher ionic concentrations of  $Mg^{2+}$  and  $Ca^{2+}$  had higher levels of AgNPs forming aggregates. The divalent cations  $Mg^{2+}$  and  $Ca^{2+}$  induced the aggregation of AgNPs more effectively than the monovalent  $Na^+$  ion, a finding consistent with a previous report (Huynh and Chen, 2011).

The degree of AgNP aggregation is also complicated by the reduction-oxidation properties of  $Ag^+/Ag^0$ , as shown in the following reaction:



Sunlight and dissolved oxygen can affect the outcomes of this redox reaction. Previous work has shown photo-transformation of AgNPs and corresponding changes

in toxicity (Cheng et al., 2011; Yin et al., 2012; Dasari and Hwang, 2013; Shi et al., 2013; Yu et al., 2014). To understand how water chemistry contributes to this process, Yin et al. (2015) also measured the photo-transformation of AgNPs in the water samples during exposure to sunlight. They irradiated the water samples in quartz glass bottles and compared them to control samples kept in the dark. They measured changes in UV-visible absorbance and characterized the morphology of AgNPs using transmission electron microscopy (TEM). They also centrifuged the water samples to separate the precipitate from the soluble  $Ag^+$  and suspended AgNPs. They determined the concentration of total silver in the supernatant (the soluble and suspended fraction) using inductively coupled plasma mass spectrometry (ICPMS). Their results showed that sunlight irradiation accelerated the transformation process and increased the precipitation of particles from AgNPs-containing samples. The greater the exposure to sunlight, the greater number of PVP-coated AgNPs underwent photo-transformation in environmental waters. Their complementary results from TEM morphology characterization of AgNPs, ICPMS detection of silver in the soluble and suspended fraction, and UV-visible absorption measurements suggest that chemical transformation, e.g., the oxidation of AgNPs and reduction of  $Ag^+$ , play an important role in the overall aggregation of AgNPs. Photo-chemical transformation, along with physical aggregation, contributes to the transfer of AgNPs from water to precipitates.

Dissolved organic matter (DOM) present in natural waters affects both the aggregation and the photo-transformation processes of AgNPs. Yin et al. (2015) have found that DOM could nullify the photo-induced aggregation (or fusion) of AgNPs. Their TEM results of morphology changes suggested a possible mechanism that involved dissolution, reduction, fusion, growth, and aggregation (Yin et al., 2014). When the dissolved  $Ag^+$  ions were reduced to  $Ag^0$  on the surface of the adjacent AgNPs that were brought together by the monovalent and divalent ions, new chain- or network-like nanostructures could be formed. This “fusion” and aggregation could result in sedimentation of AgNPs. However, DOM could disperse AgNPs. Thus, reduction of  $Ag^+$  ions to  $Ag^0$  on the surface of individually dispersed AgNPs could only result in enlarged AgNPs, but not the fused or chain-like nanostructure (Zhang et al., 2015). Results were consistent with these explanations. Certain water bodies examined by Yin et al. (2015), such as the Chaobai River, were especially abundant in DOM and as a result, less AgNP aggregation occurred. The hydrated diameters of the AgNPs remained low, and sunlight had the least effect in transferring AgNPs from water to precipitates.

The crux comes down to variation in water chemistry: each body of water has different properties that affect the aggregation and photo-transformation of AgNPs. These processes influence the transport and toxicity of AgNPs in aquatic environments. Aggregation of AgNPs could enhance the retention of AgNPs in porous media (Liang et al., 2013; Mitzel and Tufenkji, 2014), decrease their mobility, diminish transformation, decrease biological uptake (Levard et al., 2012), and potentially reduce their toxicity (Zook et al., 2011; Johnston et al., 2010). Photo-induced transformation of AgNPs could accelerate their aggregation and morphological changes. Sedimentation of larger agglomerates of

AgNPs results in the transfer of AgNPs from surface water to sediment, in which case benthic organisms would be most affected.

As nanoparticles become more commonly used, understanding their fate and behavior in relation to their aquatic environment (water chemistry) is paramount in assessing ecological hazard and public safety. The combined effects of ionic strength, DOM, dissolved oxygen, suspended particulate matter, and sunlight on the physical and chemical transformation of AgNPs in natural waters remain to be studied. In this regard, microcosm and mesocosm experiments will be useful to investigate the roles of the combined environmental factors on the fate of AgNPs and other silver species. New analytical techniques, such as the use of stable isotope tracers of  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ , could be useful in studying the inter-conversion of AgNPs and  $\text{Ag}^+$ . These stable isotopes ( $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ ) could be used to enrich  $\text{Ag}^+$  and AgNPs, respectively. By detecting  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  separately using mass spectrometry, one would be able to monitor the transformation of  $\text{Ag}^+$  and AgNPs and to evaluate the kinetics of oxidation of AgNPs and reduction of  $\text{Ag}^+$ .

Is the aggregation of silver nanoparticles in environmental waters a silver lining? The answer is not simple. Clearly, however, the aggregation and photo-transformation of AgNPs are complicated and could be more significant than previously thought. The difference in the water chemistry that controls the aggregation and photo-transformation of AgNPs results in the varying behavior and fate of AgNPs among different water bodies.

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