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Corrosion processes of triangular silver nanoparticles compared to bulk silver

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Abstract

Excessive corrosion of silver nanoparticles is a significant impediment to their use in a variety of potential applications in the biosensing, plasmonic and antimicrobial fields. Here we examine the environmental degradation of triangular silver nanoparticles (AgNP) in laboratory air. In the early stages of corrosion, transmission electron microscopy shows that dissolution of the single-crystal, triangular, AgNP (side lengths 50-120 nm) is observed with the accompanying formation of smaller, polycrystalline Ag particles nearby. The new particles are then observed to corrode to Ag₂S and after 21 days nearly full corrosion has occurred, but some with minor Ag inclusions remaining. In contrast, a bulk Ag sheet, studied in cross-section, showed an adherent corrosion layer of only around 20-50 nm in thickness after over a decade of being exposed to ambient air. The results have implications for antibacterial properties and ecotoxicology of AgNP during corrosion as the dissolution and reformation of Ag particles during corrosion will likely be accompanied by the release of Ag⁺ ions.

Keywords

Nanoparticle, plasmonics, corrosion, silver

Introduction

There is considerable interest in the properties of silver nanoparticles (AgNP). This is motivated by their current and potential applications across a diverse range of health and engineering fields. Use of colloidal Ag for health related applications has a long history (Alexander 2009) but, more recently, AgNP have found applications in wound and burn dressings, in medical instruments and implants, in fabrics for odour reduction, and in wide array of consumer products and cosmetics (Chernousova and Epple 2013; Marambio-Jones and Hoek 2010; Reidy et al. 2013). AgNP also have potential for plasmonic applications as they have an exceptionally strong plasmon response (Pastoriza-Santos and Liz-Marzan 2008; Rycenga et al. 2011). This response is exploited for surface enhanced Raman spectroscopy (SERS), an analytical technique of great sensitivity (Fan and Brolo 2009).

Triangular nanoplates of Ag are attractive for optical applications as they can be readily synthesized and display a number of well-developed dipole and multipole plasmon resonances (Fletcher et al. 2015; Keast et al. 2016; Yang et al. 2009). The multipolar resonances are excited at smaller particle sizes, relative to the situation for spheres or rods, due to the lower symmetry of the triangles. The wavelengths at which these resonances occur can be readily tuned by adjustment of their shape (Kelly et al. 2003). In addition, Ag nanotriangles in the tip-to-tip configuration (the so-called ‘nano-bowtie’) present a powerful platform for developing SERS applications spectroscopy due to the strong electric field between the tips (Kinkhabwala et al. 2009).

However, the potential of AgNP in practical plasmonic devices has not yet been fully realised due to their rapid corrosion in ambient air. The corrosion process of AgNP will also play an important role in their effectiveness in medical and antibacterial applications and may be of significance in resolving some of the inconsistencies reported in regard to antimicrobial action in real-world situations when compared to in vitro studies (Marx and Barillo 2014; McQueen et al. 2013; Storm-Versloot et al. 2010; Toy and Macera 2011; Walter et al. 2014). Additionally, an understanding of the corrosion of Ag is also necessary for the conservation and restoration of historical and cultural objects. From an environmental perspective, the growing use of AgNP in wide variety of medical, technical and consumer products gives rise to significant concerns about their ecotoxic effects upon their later release to the environment (Reidy et al. 2013). The nature, extent and time-frame of the corrosion process will be of critical importance for evaluating these environmental impacts.

A corrosion layer of Ag₂S forms on bulk Ag in normal laboratory air and does not form in a dry nitrogen environment. The formation of an Ag₂S corrosion layer requires the presence of both oxygen and water vapour and the growth rate depends on the environment (Bennett et al. 1969; Burge et al. 1969; Kleber et al. 2008; Pope et al. 1968). Atmospheric corrosion is principally by H₂S and OCS (carbonyl sulphide) (Franey et al. 1985) although corrosion by organic sulfur species has also been observed (Sinclair 1982). The corrosion has been observed to form initially as a discontinuous layer of spherical particles where the particles increase in size but not density as the corrosion proceeds (Bennett et al. 1969; Burge et al. 1969; Kleber et al. 2008; Pope et al. 1968).

The antimicrobial properties of Ag are believed to be predominantly related to the release of Ag^+ ions, which is enhanced by the relatively large surface area of AgNP when compared to the bulk form (Le Ouay and Sellacci 2015; Rizzello and Pompa 2014; Xiu et al. 2012). The sulfidation of AgNP has been observed to produce a dramatic reduction in the antibacterial effects (Reinsch et al. 2012) as the limited solubility of Ag_2S means the release of Ag^+ ions will be very slow once transformation has occurred. The Ag^+ ion release and antimicrobial effect is enhanced for AgNP with structural defects (Munusamy et al. 2015) and for flat triangular AgNPs (Lu et al. 2015; Pal et al. 2007). While corrosion is also enhanced at defects, it is slower on the $\{111\}$ planes that dominate the flat triangular Ag-NP structures and so further insight into the relationship between Ag-NP structure and corrosion is needed (Allpress and Sanders 1964; Miwa and Watanabe 1947; Philips 1962; Shiojiri et al. 1969).

The intentional and environmental sulfidation of AgNP has been extensively studied and a variety of effects have been observed (Andrieux-Ledier et al. 2013; Cao and Elsayed-Ali 2009; Chen et al. 2008; Chen et al. 2013a; Elechiguerra et al. 2005; Huang et al. 2014; Levard et al. 2012; Levard et al. 2011; Liu and Ma 2011; Lu et al. 2015; Mayousse et al. 2015; McMahon et al. 2005; Park et al. 2012; Thalman et al. 2014; Theodorou et al. 2015; Wang et al. 2011; Zeng et al. 2011). The corrosion product has been observed as an inhomogeneous Ag_2S shell around the particles, (Chen et al. 2013a; Chen et al. 2013b; Elechiguerra et al. 2005) or as the formation of separate, smaller Ag_2S particles on the surface or nearby (Chen et al. 2013a; Chen et al. 2013b; Elechiguerra et al. 2005; Lu et al. 2015; Wang et al. 2011). In instances of intentional sulfidation using solutions of high

Na₂S concentrations, the formation of bridges between the particles (Levard et al. 2011) or conversion at the tips and corners of particles (Huang et al. 2014; Liu and Ma 2011; Zeng et al. 2011) is observed.

It has been proposed that there are two distinct processes that can occur: oxidative dissolution of Ag to Ag⁺ followed by precipitation as Ag₂S; or direct conversion to Ag₂S. The oxidative dissolution route dominates at low S and the direct route at higher S concentrations. (Liu et al. 2011) The dissolution route has implications for antimicrobial activity because of the important role of the Ag⁺ ions in this process. In some cases, the formation of pure Ag secondary particles has been observed (Davidson et al. 2014; Glover et al. 2011; Theodorou et al. 2015) and this also occurred for bulk Ag objects (Glover et al. 2011).

It is clear that the chemical environment and atomic structure play a critical role in the corrosion process and that our understanding of the chemical transformation processes in AgNP, in particular, is incomplete. Furthermore, the observation of particulate-like reactions in the early stages of bulk Ag corrosion (Glover et al. 2011) may indicate that the corrosion processes in bulk Ag and AgNP have more in common than is commonly assumed. At the heart of both the corrosion process and the antimicrobial behaviour of Ag is the release of Ag⁺ ions and their subsequent interactions with other species in the local environment. In the present work we address these questions by harnessing transmission electron microscopy (TEM) to examine the corrosion of bulk Ag and triangular AgNP in order to provide further insight into this complex process.

Experimental

Bulk Ag Sheet

The bulk specimen was a 100 μm thick 99.999% pure Ag sheet (Alfa Aesar). It had been previously used to prepare TEM specimens for another study and had since been stored in a variety of office and laboratory environments for over 10 years. As a consequence of handling and long-term storage it had developed an obvious corrosion layer typical of that observed on bulk Ag objects (see the photograph of Fig. 1a). A section from the boxed area indicated was removed and sandwiched between pieces of single crystal Si wafer. A cross-sectional TEM specimen was then prepared by mechanical polishing, dimpling and ion-beam milling. A nearby area was removed for observation in the scanning electron microscope (SEM) in order to determine whether the regions displaying the different colors of the corrosion layer showed any microstructural differences.

Flat Triangular AgNP

Samples of flat triangular AgNP were prepared by reacting AgNO_3 and with NaBH_4 , using polyvinylpyrrolidone as a protective surfactant, to produce nanoparticle nuclei. These were then grown in a solution containing trisodium citrate and H_2O_2 . (Tsuji et al. 2012) This produces a solution with a vibrant blue color (See Fig. 1b) where the distinctive color is due to the plasmon resonances of the triangular nanoplates. Samples for the TEM were prepared by simply dipping a holey carbon TEM grid into the solution and placing on filter paper. Separate samples were prepared at intervals of 21, 14, 7 and 3 days and immediately before observation in the TEM.

Samples were stored in ambient air in an air-conditioned laboratory and no special precautions were taken during storage. The laboratory space contained only the electron microscope and so it is not expected that there is any exposure to fumes of chemical compounds outside of what is typical for ambient air.

Electron Microscopy

Secondary electron imaging and energy dispersive X-ray spectroscopy (EDS) of the surface of the corroded Ag sheet was performed using a Zeiss Sigma VP FESEM equipped with Bruker light element SSD EDS detector. TEM imaging and EDS spectroscopy on the bulk Ag film were performed in a JEOL 2100 LaB₆ TEM. High-resolution TEM (HRTEM) lattice imaging of the AgNP was performed in a JEOL2100F TEM.

Results and Discussion

Fig. 2 shows typical TEM images of the AgNP as they corrode. Within 3 days the formation of smaller secondary particles surrounding the triangles is observed and the triangles start to lose their regular shape. After 7 days the number of surrounding particles has increased and the shape of the triangles is further modified. By 14 days the triangles are almost fully corroded with only the occasional remnants of triangular particles remaining. Some regions of dark contrast are also observed, associated with some Ag that has not been completely converted to Ag₂S. Even after 21 days small regions of unconverted Ag still remain. The different contrast in the background for

samples at 0 days arises because an area in which the particles were hanging over the edge of the carbon support film was chosen.

Fig. 3 shows a HRTEM image of a small secondary particle observed after 3 days exposure, taken from the region as indicated by the boxed region in Fig. 2, along with the accompanying fast Fourier transforms (FFT). Similarly, Fig. 4 shows HRTEM and FFTs for the boxed particles after 7 days exposure. At 3 days, the small newly formed particles are observed to be predominantly fine-grained particles having a lattice spacing consistent with pure Ag. At 7 days exposure some of the small particles have started to convert to Ag₂S, as lattice spacings consistent with of the Ag₂S appear, such as the {111}, {-1-12} and {120} planes (3.08 Å, 2.84 Å and 2.66 Å respectively). The sulfidation is associated with a distinctive dual-contrast appearance of the secondary particles, consisting of a dark area where the lattice spacing is consistent with the Ag fcc lattice and lighter “lobes” that appear amorphous or have lattice spacings consistent with Ag₂S. The presence of S in the corroded AgNP has also been confirmed with EDS.

The flat triangular AgNP have a distinctive 2.5 Å spacing which has been associated with a $\frac{1}{3}\{422\}$ reflection arising from internal stacking faults (Kirkland et al. 1993). Even as the triangles corrode, their distinctive appearance is not significantly altered. This is illustrated in Fig. 5, which is a composite image showing a corroded triangle after 7 days exposure accompanied by smaller very fine-grained polycrystalline Ag particles (as indicated by the Ag{111} ring in the FFT). Some of

these are partially converted to Ag_2S and the FFT reveals spots that have lattice spacings that are consistent with Ag_2S and are larger than the largest possible lattice spacing in fcc Ag.

At 14 and 21 days exposure, the observed lattice spacings of the particles are predominately from Ag_2S , but small kernels of polycrystalline Ag still remain. Fig. 6 shows an example of a corroded triangle after twenty-one days exposure, where the original triangular shape can still be distinguished and small amounts of unconverted Ag remain.

Fig. 7a-c show TEM images of the cross-section of the corrosion layer from different areas of the bulk Ag sample. This is the first time, to our knowledge, that cross-sectional images of the corrosion of bulk Ag has been observed. The layer was on the order of 20-50 nm thick and has an inhomogeneous, particulate nature that is not markedly different than that observed as shell around AgNP in previous work (Chen et al. 2013a; Chen et al. 2013b; Elechiguerra et al. 2005). The particulate nature of the layer is also obvious in the SEM image of Fig. 7d. SEM images taken from different regions of the surface, where the corrosion layer had a different color, were indistinguishable. The EDS spectra taken in the SEM showed only the presence of Ag and S. The regions where the corrosion layer was darker had a higher relative S concentration, indicating the corrosion layer was thicker at that point, as expected. Fig. 7e shows an annular dark field image acquired in scanning TEM mode. The brightness is related to the average atomic number of the materials and so the bulk Ag corresponds to the bright regions, the medium grey to the Ag_2S

corrosion layer and the dark areas to the sample adhesive. The corresponding map of the intensity of S peak in the EDS spectrum shown in Fig. 7f confirms this interpretation.

There are also much smaller small particles of around ~5 nm in size observable in some of the TEM images of the bulk sample, including on the sample adhesive. It is quite likely that these are an artefact produced by redeposition during the ion milling process and it would not be justified at this stage to interpret these as secondary particles formed during the bulk corrosion process. However, the clear particulate nature of the corrosion layer raises the possibility that the corrosion of bulk Ag may also proceed by the dissolution and reprecipitation of secondary Ag particles that are then later converted to Ag₂S. Further work is required to clarify the role, if any, of the formation of small secondary particles in the corrosion of bulk Ag. This work has demonstrated the potential of cross-sectional TEM to examine the corrosion process of bulk Ag and in future work we propose to turn our attention to examine the early stages of the corrosion process. However, there is some indication here that the corrosion process for bulk Ag is not fundamentally different from the AgNP.

The ubiquitous presence of stacking faults in the triangular AgNP may have an important role in both their corrosion and their antibacterial effects. The particles were observed to predominantly corrode from the edge inwards with the release of Ag⁺ ions which migrate away from the triangle and reprecipitate as small polycrystalline particles. The presence of the stacking fault defects intersecting with the surface at the triangle edges may accelerate the ion release at these locations.

The accelerated ion release when defects intersect the surface can also explain the accelerated corrosion previously observed at the tips of nanorods, as these particles can have a multi-twinned internal structure with defects running along the length of the rod and intersecting at the surface of the tip (Chen et al. 2015; Chen et al. 2013a; Elechiguerra et al. 2005).

The effect of capping agents on the Ag{111} surface has been described as accounting for the different corrosion rates for different parts of the AgNP (Chen et al. 2013b). However, Ag⁺ ions have been observed to be able to migrate through thick carbon coatings (Bokhonov 2014) whereas the high coordination number of the Ag{111} surface may slow the ion release (Allpress and Sanders 1964). The small polycrystalline secondary nanoparticles are converted to Ag₂S much more quickly than the parent AgNP under the exposure conditions used here and this can be attributed to their highly defected structure.

In this work the AgNP have been deposited on an amorphous carbon substrate of the TEM grid and this is likely to play an important role in the accelerated corrosion in comparison to bulk Ag. The presence of a microscopic layer of H₂O on the surface of the substrate provides a medium in which the Ag⁺ ions can migrate away from the particles, allowing for further release and migration. It is not expected that the nature of the substrate would make a substantial difference to this process unless it was particularly hydrophobic. In the case of bulk Ag, in the absence of a migration pathway, the released ions will remain in an environment of high Ag⁺ concentration which is likely to slow the release of further ions. For the same reasons, when suspended in an aqueous

environment, very rapid dissolution of the original AgNP will occur. In that case the final destination of the released ions will depend critically on the chemistry of the solution.

Conclusions

In this work we have demonstrated that there are three (not two as previously discussed) possible mechanisms that must be considered for the corrosion of AgNP and possibly bulk Ag:

- (1) direct conversion to Ag_2S .
- (2) oxidative dissolution of Ag to Ag^+ followed by precipitation as Ag_2S .
- (3) oxidative dissolution of Ag to Ag^+ followed by precipitation as nanoparticulate Ag, then followed by conversion to Ag_2S .

Which of these processes dominate will be determined by the local environment. It is possible that some of the previous observations in the literature of the formation of Ag_2S particles were preceded by the formation of the Ag particles that then subsequently transformed to Ag_2S before observation (Chen et al. 2013a; Chen et al. 2013b; Elechiguerra et al. 2005; Lu et al. 2015; Wang et al. 2011). In addition to the presence of water, oxidising species, and the concentration of available S ions, the exposure to light will also be significant in determining which corrosion process will dominate. The photoinduced conversion of Ag nanoparticles into small clusters by the interaction with light is well-established (Jin et al. 2001). The release of Ag^+ ions, the availability of a substrate on which they can migrate away from the parent Ag-NP, and their reprecipitation and transformation to Ag_2S are all important factors controlling their corrosion and antimicrobial properties. The results

presented here demonstrate that, despite considerable work to date, it is clear that many questions about the corrosion of Ag, in both nanoparticle and bulk form, are yet to be resolved.

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Fig. 1. (a) Photograph of a corroded Ag sheet. Circular areas where sections were removed for previous (unrelated) studies can be seen. The box indicates the region of the sheet selected for study here. (b) Photograph of the solution containing flat triangular AgNP. The brilliant blue colour arises from the excitation of plasmon resonances.

Fig. 2. TEM images of the corrosion of flat triangular AgNP for different lengths of time exposed to ambient laboratory air. HRTEM images of the boxed regions are given in Figs. 3 and 4.

Fig. 3. (a) HRTEM image of secondary particles formed near a flat triangular Ag-NP after 3 days of exposure to laboratory air. The image corresponds to the boxed region of Figure 2. (b) The FFT of part of the triangle reveals spots associated with the $\frac{1}{3}\{422\}$ reflection that are characteristic of triangular nanoplates. (c) The FFT of the smaller particle shows spots corresponding to the $\{111\}$, $\{002\}$ and $\{220\}$ planes of Ag.

Fig. 4. (a) HRTEM image of secondary particles formed near a flat triangular Ag-NP after 7 days of exposure to laboratory air. The image corresponds to the boxed region of Figure 2. (b) The FFT of the entire region reveals spots associated with the $\frac{1}{3}\{422\}$ reflection that are characteristic of triangular nanoplates, spots associated with the $\{111\}$ planes of Ag and larger lattice spacings that can be identified as coming from regions of Ag₂S.

Fig. 5. (a) HRTEM image of secondary particles formed near a flat triangular Ag-NP after 7 days of exposure to laboratory air. (b) The FFT of the smaller particles shows a ring corresponding to the $\{111\}$ planes of Ag as well as additional spots corresponding to the larger spacings of Ag_2S . (c) The FFT of the corroded triangle shows that the characteristic $\frac{1}{3}\{422\}$ reflections are unchanged.

Fig. 6. (a) TEM image of the remnants of a flat triangular Ag-NP after 21 days of exposure to laboratory air. (b) The HRTEM image shows a kernel of remaining fine-grained polycrystalline Ag with the remainder fully converted to Ag₂S. (c) The FFT shows a ring corresponding to the {111} planes of Ag as well as additional spots corresponding to the larger spacings of Ag₂S.

Fig. 7. (a)-(c) TEM cross-sectional images of the corrosion layer formed on a bulk Ag sample after over 10 years exposure to ambient indoor environments. (d) SEM image of the surface of the corrosion layer. (e) Annular dark field image of the corrosion layer (medium gray area) with (f) corresponding EDS map of the S content.