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At all length scales, the stability or programmed instability of a material in a given environment is important both for its use in applications as well as its environmental impacts downstream. A first step in understanding the deterioration of coinage metal nanoparticles is to leverage knowledge from bulk coinage metal reactivity. These studies highlight fundamental chemical forces (both intrinsic to the material and extrinsic from the environment) that influence the rate, morphology, and chemical composition of deterioration products. For nanoparticle deterioration, both environmental and intrinsic particle factors must be considered. In concert, these factors can lead to modes of nanoparticle deterioration that are different from their bulk counterparts and are important to consider when designing and implementing these new materials.

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Connecting Concepts of Coinage Metal Stability Across Length Scales

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At all length scales, the stability of materials is impacted by their surrounding environment. However, it has now been observed that materials with different dimensions can exhibit markedly different responses to their environment, even for the same material composition. For example, the deterioration of nanomaterials is complicated by the unique chemical and physical properties that arise from changes to their size, shape, and/or surface chemistry. A first step in understanding and predicting nanomaterial stabilities is to leverage the decades of work dedicated to understanding the environment-specific deterioration mechanisms of analogous bulk materials. Then, unique nanoscale properties can be accounted for and used to understand both similarities and differences in deterioration behavior across these length scales. In this review, we specifically consider the stability of Group 11 coinage metal surfaces: copper, silver, and gold. We first summarize the chemical mechanisms of environmentally-driven deterioration of these metals in the bulk. We then apply this knowledge to interpret stability studies of nanoparticles made from the same elements. Ultimately, we find that while the reactivity of gold and copper are relatively consistent across length scales, the composition of products formed on silver surfaces differs significantly. These results have important implications for predicting and controlling both desirable and undesirable metal nanoparticle deterioration processes.

1. Introduction

Metal nanoparticles (NPs) are now widely used and/or tested in a variety of consumer products[1] and biomedical technologies.[2, 3] The efficacy of NPs in these technologies relies on either their stability or programmed instability.[4] For example, for gold (Au) NPs used in cancer treatment, preservation of NP size, shape, and surface chemistry is crucial to their targeting and performance as ablation agents. On the other hand, for consumer products containing silver (Ag) NPs, it is known that release of Ag(I) ions from the particles plays a key role in their antimicrobial properties. Therefore, there has been a significant effort to determine the factors that influence the reactivity of, and ion release from, metal NPs.

Of course, surface chemical transformations are not unique to the nanoscale and indeed strongly influence the performance of metals in a wide variety of applications ranging from water pipes to antimicrobials. For example, it has been known for centuries that bulk metals exposed to various environments can react by forming surface films and/or dissolving. By combining what we know about these bulk reaction pathways with the unique criteria that influence metal surface reactivity at the nanoscale (e.g. surface energy and ligand chemistry), we can establish an understanding of the environmental and materials properties that influence NP surface stability. Then, we can leverage these insights to create tailored, safe, and sustainable NPs with either programmed stability or instability, as the application demands.

In this review, we first discuss the decades of work studying bulk metal surface reactivity (often termed broadly in the materials science literature as "deterioration"), and specifically the reactivity of coinage metal surfaces (here: Ag, Cu, and Au). We choose these metals because they represent a large fraction of the metal NPs that have been widely studied and tested for possible applications.[3, 5-9] We then review how specific NP properties influence the translation of bulk metal deterioration chemistry to the nanoscale. Specifically, we discuss both intrinsic NP properties (e.g. NP size, shape, and surface chemistry) as well as extrinsic environmental factors (e.g. pH, ionic strength) that influence the dominant surface reactivity mechanisms observed in metal NPs.

2. Deterioration of Bulk Metals

By definition, materials in use encounter their surrounding environment. These interactions frequently lead to chemical changes in the original material and are termed broadly as material deterioration (often regardless of whether the chemical transformation is desired or undesired).[10-12] Understanding, mitigating, and/or leveraging deterioration mechanisms is crucial to the performance of all materials and has been studied for centuries. For the metals discussed here, deterioration primarily occurs through two processes. In one process, a "scale" or film of distinct

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chemical composition from the original metal forms upon environmental exposure. These scale formation processes are classified broadly as "oxidation" in the classic literature, but also encompass other scale-forming reactions such as sulfidation.[10, 12, 13] In the other process, depending on the chemical identity and properties of the scale, the surface can dissolve or otherwise lose mass to the environment.[12, 13] For any given surface, one or both of these processes may be active. The work discussed here will demonstrate that the majority of bulk Ag deterioration can be classified as scale formation with no resulting dissolution, while the deterioration of bulk Cu includes scale formation as well as dissolution. Finally, we will show that Au does not undergo these deterioration mechanisms to a measurable degree under the conditions discussed.

Of course, the deterioration mechanisms that occur on metal surfaces are determined not only by metal identity, but also by the environment that they are exposed to. There are 4 primary environments that metals are challenged with: 1) outdoor atmosphere, 2) indoor atmosphere, 3) lab-controlled atmosphere, or 4) solution conditions (both wild and laboratory). Atmospheric tests (both indoor and outdoor exposures) demonstrate that the following parameters are some of the most important factors in determining bulk deterioration pathways: percent relative humidity (RH), atmosphere exposure time, and identity/concentration of constituent gases.[13] For each of these, ambient temperature and pressure (and other location-specific conditions) can also influence deterioration outcomes, and this is most often seen when testing samples under similar conditions but different geographic locations (*vide infra*).[14, 15]

Although many of the studies discussed in this review are carried out in standard atmospheric conditions or lab exposures intended to mimic standard atmospheric conditions, the surface of the metal is typically not directly interacting with the atmospheric gases. Instead, depending on the RH, there are a few monolayers (MLs) of water adsorbed to the metal surface. The number of adsorbed monolayers on a surface varies from about 1 ML at 20% RH to about 5-10 MLs at 80% RH.[13, 16-18] The water provides a medium for atmospheric gases to adsorb/dissolve and react with the metal surface.[13, 16, 19] Due to the adsorbed water, deterioration processes generally occur at a solid/liquid interface even if the material is not immersed in an aqueous solution. In the following section, we will discuss the deterioration of bulk Ag, Cu, and Au through scale formation and dissolution mechanisms.

2.1 Bulk Silver

Silver is widely used in consumer products, including jewellery, decorative objects, silverware, batteries, electronics, and dental fillings.[13] Here, we will discuss bulk Ag surface reactions with atmospheric pollutant gases as well as with various oxygen species. The deterioration of Ag in aqueous environments such as sea water and waste treatment streams is also relevant, but the exposure of bulk Ag to these wet environments is much less studied and indeed more prevalent for AgNP exposures (*vide infra*).

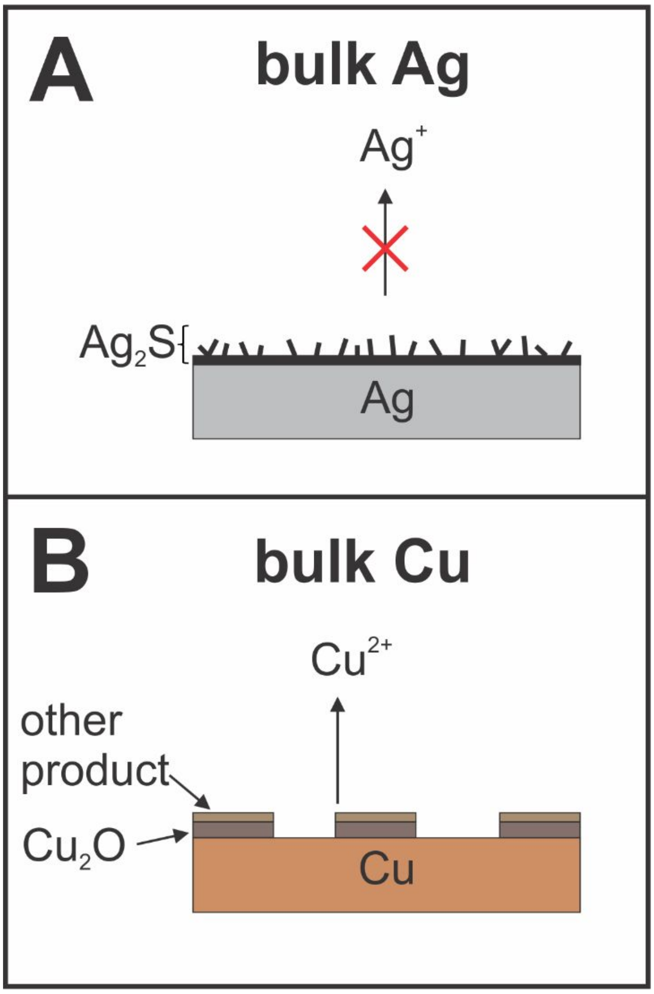

Figure 1. Summary of the most prevalent deterioration processes that occur for bulk Ag and Cu (not to scale).

2.1.1 Scale Formation on Silver Caused by Atmospheric Pollutants.

Under normal atmospheric conditions, Ag does not react primarily with oxygen, but instead reacts with minority, pollutant gases. The most commonly studied atmospheric pollutants for Ag deterioration are H_2S, carbonyl sulphide (COS), Cl^- (from either gaseous HCl or particulate NaCl), SO_2, and NO_2 (Table 1). If only H_2S or COS is present, Ag_2S forms,[20-28] while if only Cl^- or Cl_2 is present, AgCl forms.[29, 30] However, if multiple pollutant gases are present, such as in a realistic indoor or outdoor environment, Ag_2S is generally found to be the most abundant or only product (Figure 1A),[16, 28, 31-35] and importantly, the formation of Ag_2S is not determined by the relative abundance of the sulphur-containing gases (Table 1). Instead, the abundance of a particular deterioration product is largely determined by its solubility. Because Ag_2S is exceptionally insoluble ($K_{sp} = 6 \times 10^{-51}$),[36] it is generally the most abundant product.[16] However, there have been some studies that show AgCl can form in higher abundance than Ag_2S when high concentrations of Cl^- are present.[14, 32, 37, 38]

The reaction of Ag with H_2S is proposed to be:[26, 28, 39, 40]

$$2Ag + H_2S + 1/2O_2 \rightarrow Ag_2S + H_2O$$

Table 1. Common atmospheric pollutants for Ag and Cu.

Pollutants	Indoor Sources	Outdoor Sources	Approximate Indoor Concentration (ppb)	Approximate Outdoor Concentration (ppb)	References
H_2S	Outdoor air brought indoors, cooking	Marshes, volcanoes, crude oil processing, paint and rubber aging, human waste, organic decay, paper mills, fossil fuel combustion	0.1 – 0.7	Remote area/background: 0.005 – 0.5	10, 13, 14, 16, 19, 21, 24, 41-44
COS	Wool, biofuel combustion	Microbial activity, volcanoes, oceans, soil, fires, industry, biomass burning	0.3 – 0.6	Remote area/background: 0.3 – 0.6 Urban/industrial/near source: 0.3 – 0.6	14, 16, 21, 41, 44-47
Cl^- (from either HCl or NaCl)	Cleaning products, PVC degradation	Fossil fuel combustion, water treatment, insecticides, ocean spray, volcanoes, burning of synthetic products	0.1 – 0.4	Urban/industrial/near source: 0.5 – 100	10, 13, 14, 16, 19, 42
SO_2	Space heaters, outdoor sources	Fossil fuel combustion, metal smelting	0.2 – 30	Remote area/background: 0.05 – 0.12 Urban/industrial/near source: 1 – 1000 Average across US: 1 – 71	13, 14, 16, 19, 21, 24, 41-43, 48
NO_2	Space heaters, cooking, decomposition of nitrocellulose (wood coating and book cloth binding)	Oxidation of NO during fossil fuel combustion, smog	2 – 250	Urban/industrial/near source: 0.5 – 300 Average across US: 11 – 85	13, 14, 16, 19, 42, 43
$(NH_4)_2SO_4$ (from reaction of NH_3 + oxidized SO_2)	NH_3: cleaning products	NH_3: agriculture, airborne particulates, organic decay, combustion, fertilizer plants	NH_3: 10 – 216	Urban NH_3: 1 – 90 Average across US NH_3: 9 – 17	10, 13, 16, 19, 42, 48-50
Organic acids	Wood, glue, varnish	Wood, incomplete combustion of wood or other vegetation, reactions of photochemical smog	10 – 20	Urban/industrial/near source: 0.5 – 30	10, 13, 16, 43

The evidence for this reaction (as opposed to $2Ag + SH^- \rightarrow Ag_2S + 1/2H_2$) is that the rate increases in the presence of oxygen[26] and no hydrogen is formed.[40] The proposed mechanism indicates that the H_2S does not react with the Ag surface directly; instead H_2S reacts with O_2 to form free sulphur, which then reacts with the Ag to form Ag_2S.[40, 51] The presence of other gases, such as SO_2 and NO_2, in combination with H_2S can also initiate the formation of free sulphur which then reacts with Ag to form Ag_2S.[26-28, 35, 52]

As discussed above, the RH determines the amount of water adsorbed to the metal surface, which is the medium for adsorption and reaction of the pollutant gases. As a result, most studies find that scale formation on Ag increases with increasing relative humidity.[14, 20, 26, 27, 32, 51] Although there are some studies that report RH does not impact scale formation,[14, 19, 26, 34, 53] these apparent contradictions can be explained by the specific experimental conditions in each case. For example, in one study it is hypothesized that water is not needed at the surface when free sulphur is already present and can react directly with the surface.[53]

In addition to the chemical identity of the scale, the scale morphology can also influence the performance of bulk Ag. When pollutants react with a Ag surface, the scale has been shown to form various architectures including dendrites, spikes, whiskers, and needles.[16, 17, 22-24, 31, 39, 51, 53, 54] These scale architectures can be problematic. For example, the formation of non-uniform architectures has been shown to cause short circuits in Ag-based electrical materials.[17, 54]

Because of these performance issues and also because of the undesirable aesthetics of scales on bulk Ag surfaces, it is often desirable to remove the scale layer. There are three main categories of treatments that can remove scales from a Ag surface: mechanical, chemical, and electrochemical.[44] Mechanical cleaning involves using tools or abrasive compounds such as $CaCO_3$, Al_2O_3, or SnO_2. Chemical cleaning most commonly uses a reaction with chemicals such as acetic acid, ammonia, or thiourea to dissolve scale products. Electrochemical cleaning can use methods such as galvanic reduction, an added reducing agent, or a potentiostat to reduce the oxidized product(s). Finally, it has also been shown that the formation of Ag scales can be slowed or prevented by modifying the surface of the Ag using molecular adsorbates. For example, surface-adsorbed molecules such as poly(3-amino 1,2,4-triazole),[55] polyaniline,[56] or self-assembled monolayers of molecules such as hexadecanethiol[55, 57] or perfluoroalkyl amideethanethiols[58] are known to prevent or slow Ag scale formation.

2.1.2 Scale Formation on Silver Caused by Oxygen. Up to this point, we have discussed the interaction of bulk Ag with pollutant gases present in Earth's atmosphere. In those experiments, gases such as N_2 and O_2 are also present, but the deterioration products are dominated by minority gases such as COS, H_2S, and/or halide-containing species (*vide supra*). Therefore, scale products such as nitrates and oxides are not commonly observed. However, in the *absence* of competing reagents (such as the pollutants described above), gases such as atomic oxygen and ozone can oxidize bulk Ag surfaces and produce silver oxide scales. Much of the work that has been done to characterize the behaviour of oxygen species on bulk Ag surfaces has been for the purpose of elucidating the mechanism for Ag-catalysed epoxidation of ethylene.

When bulk Ag is exposed to O_2 only, Ag_2O does not necessarily form due to the low dissociative sticking probability of O_2 on Ag. Here, the sticking probability is defined as the ratio of the number of surface-adsorbed atoms (or molecules) to the total number of atoms (or molecules) that the surface is exposed to. For O_2 on Ag, the sticking probability is reported to be between ~10^{-3} – 10^{-6}.[59-66] (It is important to note that this adsorption probability is facet-dependent. The O_2 sticking probability for Ag(111) surfaces (~10^{-6}) is two orders of magnitude lower than for Ag(110) surfaces (~10^{-4}).[60, 61, 63, 64, 67-70]) The low sticking probability leads to a low concentration of dissociatively-adsorbed oxygen atoms on the Ag surface. The concentration is low enough that the dissociatively-adsorbed oxygen is not a source of Ag oxidation at ambient temperature and pressure.[69, 71, 72] Instead, at low surface coverages of dissociatively-adsorbed oxygen atoms, chemisorption of those oxygen atoms is thermodynamically favoured over Ag_2O formation, as the enthalpy of atomic oxygen adsorption (-177.2 kJ/mol O_2) is lower than the enthalpy of formation of Ag_2O (-60.6 kJ/mol O_2).[61, 68, 69] For Ag oxidation to occur, a critical coverage of oxygen atoms (generated from dissociative adsorption of O_2 or even NO_2 at high temperatures) must be reached (~0.05 – 0.08 ML),[61, 70] at which point the formation of Ag_2O becomes the more thermodynamically favourable process[69] and the reaction is:[73, 74]

$$4Ag(0) + O_2 \rightarrow 2Ag_2O$$

The situation is different when Ag is exposed to atomic oxygen itself instead of O_2. Silver oxidation readily occurs, and the oxide identity ($Ag^IAg^{III}O_2$ vs. Ag_2O) depends on the temperature. There is some variation in the reported temperatures at which these species form, but at approximately room temperature or below, $Ag^IAg^{III}O_2$ is observed,[73, 75, 76] while at room temperature or above, Ag_2O is observed.[72-74, 77-80] We note that in addition to O_2 and atomic oxygen, ozone can also oxidize Ag by dissociative adsorption to the Ag surface (sticking probability ~1),[69] which produces $Ag^IAg^{III}O_2$ and/or Ag_2O.[30, 69, 71, 81]

For all cases of oxygen reacting with a Ag surface, the RH of the environment can influence the mechanism and extent of the chemisorption and/or oxidation processes.[30, 38, 82, 83] For example, under dry conditions, O_2, atomic oxygen, or ozone can interact directly with the Ag surface.[30, 38, 82, 83] However, under wet conditions, O_2 and atomic oxygen do not react with the Ag surface directly, but instead can react with the adsorbed water to form hydroxyl radicals which then react with the Ag surface.[30, 38, 83]

Importantly, the stability of the Ag oxide scale is also strongly influenced by whether there is adsorbed water on the surface. In water, Ag_2O is only stable at high pH (~13 – 14) and oxidizing potentials (~0.3 – 0.5 V),[16] leading to its dissolution in oxygenated water at a rate of 0.002 nm/min (but can be as high as 2100 nm/min at more anodic potentials).[56]

Finally, we reiterate that for all of the experiments discussed in this section, the conditions are highly controlled and Ag surfaces are specifically exposed to either O_2, atomic oxygen, or ozone. However, under standard ambient conditions, the adsorption of O_2 on bulk Ag is outcompeted by sulphur-containing gases to form Ag_2S due to a combination of the extremely low solubility of Ag_2S, the low dissociative sticking probability of O_2 on Ag, and the low stability of Ag_2O in water (*vide supra*). As a result, Ag oxides are not typically observed on environmentally-exposed bulk Ag.

2.2 Bulk Copper

Copper is used in a wide variety of applications including pipes, architecture, sculptures, and electronics.[11, 13] Although the majority of bulk Ag corrosion studies were carried out in atmospheric conditions, the corrosion of bulk Cu surfaces has been studied in both atmospheric conditions and aqueous solutions.

2.2.1 Scale Formation on Copper Caused by Atmospheric Pollutant Gases. Scale formation on bulk Cu is observed in atmospheric conditions, where a patina forms on the Cu surface over the course of years. Unlike Ag, where there is generally a single scale product (Ag_2S), the exposure of Cu to atmospheric conditions can result in the formation of multiple products, depending on the exposure time, environmental conditions, and relative concentrations of atmospheric pollutants.[84]

In ambient air, Cu_2O forms,[14, 15, 19, 31, 32, 84-92] generally before the formation of CuO, $CuO{\bullet}H_2O$, $Cu(OH)_2$,[86, 89] or other products (Figure 1B, *vide infra*).[11, 15, 84-86] The sticking probability of O_2 on Cu surfaces is reported to be between 10^{-3} – 1.0, which is orders of magnitude higher than on Ag (*vide supra*).[93-97] Thus, Cu_2O forms more readily than Ag_2O, although the initial oxygen chemisorption and oxide island nucleation must still occur and reach a critical coverage before Cu_2O can form.[61, 96, 98-102]

Unlike in the case of Ag, Cu_2S is rarely observed in ambient conditions, since the formation of Cu_2S requires the presence of Cu(I), which is easily oxidized to Cu(II) (E^o = 0.153 V vs. SHE[103]).[13] Instead, CuS (which is very insoluble ($K_{sp} = 6 \times 10^{-36}$)[104]) can form when Cu is exposed to reduced sulphur compounds such as H_2S and COS.[105]

When Cu is exposed to oxidized sulphur compounds (such as SO_4^{2-}, which is a product of atmospheric SO_2 oxidation[13]), various products can form depending on the exposure time. At long atmospheric exposure times (years), $Cu_4SO_4(OH)_6$[15, 84, 87, 88, 92, 106] and $Cu_3SO_4(OH)_4$[15, 84, 88] form, and at intermediate exposure times, $Cu_4SO_4(OH)_6{\bullet}H_2O$[14, 15, 84, 85, 88, 92] and $Cu_{2.5}SO_4(OH)_3{\bullet}2H_2O$[84] are likely to form. When chloride is present at a high concentration, such as in locations near the ocean, CuCl[14] and $Cu_2Cl(OH)_3$[15, 86-88, 106] can also form (Figure 1B).

In order to more thoroughly understand the products that form during atmospheric exposures of Cu, many lab-controlled exposure studies of bulk Cu have been done with the pollutant gases listed in Table 1.[19, 20, 41, 49, 90, 91, 107-117] As with the atmospheric studies above, a variety of Cu scale products can form, depending on the exposure conditions. In many of these lab studies, Cu_2O and CuO were observed along with other products. When Cu is exposed to H_2S or COS, copper sulphide forms.[19, 20, 41] When Cu is exposed to SO_2 and/or NO_2, $Cu_{2.5}(OH)_3SO_4{\bullet}2H_2O$, $Cu_4(OH)_6SO_4{\bullet}2H_2O$, and $Cu_4(OH)_6SO_4$ form. When Cu is exposed to NaCl, CuCl and $Cu_2(OH)_3Cl$ form.[108] Interestingly, studies which exposed Cu to $(NH_4)_2SO_4$ (formed by reaction of NH_3, which is commonly found in the atmosphere, and SO_4^{2-}, which is formed when atmospheric SO_2 is oxidized[13]) found the formation of the most common products described above ($Cu_4SO_4(OH)_6{\bullet}H_2O$, $Cu_4SO_4(OH)_6$, and $Cu_3SO_4(OH)_4$). Thus, $(NH_4)_2SO_4$ is postulated to be an important component of ambient Cu scale formation.[11, 49, 110, 111, 118, 119] These studies also find that the effect of RH on Cu is similar to that for Ag, where as the RH increases, the amount and/or rate of scale formation increases as well.[19, 20, 49, 90, 107, 109, 110, 115, 116]

2.2.2 Dissolution of Copper in Aqueous Environments. Overall, the studies of atmospheric pollutants on bulk Cu are useful for describing the expected deterioration products of Cu used in applications such as indoor decorations and electronics. However, bulk Cu is also commonly used in applications where it encounters water, such as in architecture or piping. Because of these exposures, there has also been significant research effort to describe the deterioration of bulk Cu immersed in various aqueous environments.

When bulk Cu is immersed in water (e.g. tap water, distilled water, or buffered solutions), Cu_2O forms.[120-126] Under certain conditions (mainly high pH), CuO, $Cu(OH)_2$, and/or $CuO{\bullet}xH_2O$ have also been observed.[120-124] The specific solution conditions influence the formation of other copper scale products on top of the copper oxide layer (Figure 1B). For example, $Cu_4SO_4(OH)_6$ may form when SO_4^{2-} is present,[86, 118, 127] or CuCl may form when Cl^- is present[118, 128] (although $CuCl_2^-$ can also form[129]).

Complications in predicting the composition and amount of copper scale products can arise when studying Cu that is exposed to cycles of wet and dry conditions due to precipitation.[13, 84, 86, 130] When Cu is unsheltered and exposed to precipitation, both atmospheric pollutants and water-soluble products can be washed away or diluted, which may decrease the amount of scale formed. However, the precipitation could also contain ions such as Cl^- or H^+ which can increase the amount of scale formed. Thus, the overall effect of precipitation on deterioration is highly dependent on the specific conditions for each exposure.

As mentioned above, environment-exposed Cu surfaces not only form scale, but also can undergo subsequent dissolution processes (*vide infra*). Each scale product has different solubility properties. For the original bulk Cu metal, the overall dissolution reaction is:[131-133]

$$Cu + 2H^+ + 1/2O_2 \rightarrow Cu^{2+} + H_2O$$

This reaction is pH-dependent, and it has been found that as the pH increases, the bulk Cu dissolution decreases.[118, 134-136] Other species in solution, such as natural organic matter (NOM, a mixture of many different types of organic compounds formed due to the decay of plants and animals) and proteins, can also influence dissolution.[136-138]

Finally, although a scale on the surface of bulk Cu can sometimes be desirable for aesthetic purposes, these deterioration mechanisms can be inhibited by the adsorption of molecules on the Cu surface, as was the case for Ag. Molecules such as benzotriazole[139-141] and thiols[142-146] have been shown to be effective for preventing Cu scale formation in water. Thiols have also been studied for their inhibition properties in gaseous conditions.[147-150]

2.3 Bulk Gold

The deterioration of bulk Ag and Cu can be observed with the naked eye, and we have discussed this deterioration in 4 primary environments. However, bulk Au does not obviously deteriorate under standard ambient environmental conditions or even under some common, challenging environments (e.g. the human mouth during dental uses[151, 152]). Studies of Au in these environments are more limited, but they reveal that Au does not oxidize when exposed to either O_2, atomic oxygen, or pollutant gases at either ambient or higher temperatures (>700 °C).[72, 109, 153-156] This low reactivity is expected from the electronic structure of Au. Nørskov et al. summarize the impact of Au electronic structure on its low reactivity as the combination of filled states between the antibonding orbitals of the adsorbate and the Au d states, the large overlap of adsorbate and Au orbitals, and the large cohesive energy of Au.[157] The low reactivity of Au does not necessarily preclude the chemisorption of atomic and molecular oxygen to Au surfaces, but there has been disagreement in the literature as to whether or not chemisorption of molecular oxygen occurs.[156] However, bulk Au does oxidize when exposed to a low pressure Hg, ozone lamp at room temperature.[158]

2.4 Summary of Bulk Oxidation and Corrosion

Interestingly, in the bulk, the majority of Ag deterioration involves the formation of Ag_2S, which is insoluble and thus does not lead to bulk Ag dissolution. For Cu, the chemistry is much richer, and a variety of products can form, some of which can lead to Cu dissolution. Finally, in general, Au is relatively inert and does not oxidize under any of the comparable conditions discussed for Ag and Cu.

3. Deterioration of Metal NPs via Intrinsic Factors

Clearly, there is a wealth of chemical information available about the deterioration of bulk coinage metal surfaces in various environments. A key question is how nanoscale analogues of these metal surfaces do and do not adhere to the chemistry described. Unique features of nanoscale metal materials include their high percentage of surface atoms, their size-, shape-, and surface chemistry-dependent optoelectronic properties, and their degree of dispersion in a given liquid medium (i.e. aggregation state). Each of these features (either individually or in combination) may influence the deterioration chemistry of the particle surface.

Some changes in NP reactivity compared to the bulk are to be expected, and are a fundamental function of their increased surface area per unit mass. The increased surface:volume atom ratio leads to a large number of unsatisfied bonds per unit mass, which can lead to a higher solubility of the NP surface relative to a bulk surface of the same metal. The following equation (Ostwald-Freundlich) shows that relationship, where smaller NPs are predicted to exhibit a higher equilibrium solubility:

$$S_r = S_{bulk} \text{ x } \exp(2\gamma V_m/RT \text{ x } r)$$

where S_r is the solubility of NPs with radius r, S_{bulk} is the solubility of the extended metal surface, γ is the surface tension, V_m is the molar volume, R is the gas constant, and T is temperature.[159, 160]

In addition to the increase in surface solubility, the apparent redox potential of the metal can decrease as particle diameter decreases.[161-166] The relationship between the bulk potential, E^o_{bulk}, and the NP potential, E^o_P, has been described as:

$$E^o_P = E^o_{bulk} - (2\gamma V_m)/(zFr)$$

where γ is the surface tension, V_m is the molar volume, z is the valence state of the metal, F is Faraday's constant, and r is the NP radius.[164, 166] Together, these relationships indicate expected impacts of NP size on surface reactivity and deterioration.

There are two additional components of NP surfaces to consider when interpreting these fundamental solubility and reactivity relationships: the surface crystallographic features of the NP and the surface-adsorbed molecules (also called ligands). Due to the high surface energy and chemical potential of NPs, ligands are important for stabilizing the NPs through either electrostatic or steric mechanisms[159, 167] and at sufficient coverages can also control the accessibility of oxygen and other species to the particle surface.[168-170] This ligand-mediated access to the NP surface is an important factor for determining the extent of surface scale formation and any subsequent ion release. In addition, the reactivity of surface metal can be influenced by the adsorption of thiols or other nucleophiles on the NP surface, which can decrease the apparent redox potential of the metal, leading to easier oxidation.[162, 171, 172]

In the following section, we will discuss how the size, surface chemistry, and shape of Ag and Cu NPs have been shown to influence NP deterioration. The vast majority of literature examines the deterioration of metal NPs in terms of their dissolution (also called ion release).[173] There are several different methods that have been used to measure NP dissolution. Two of the most common are inductively coupled plasma mass spectrometry or optical emission spectroscopy (ICP-MS/OES) and graphite furnace atomic absorption spectroscopy (GF-AAS). Before being used, these two methods require the separation of the released ions from the NPs, typically by centrifugation (with or without the use of molecular weight cut-off filters). Other methods such as absorption spectroscopy or ion-selective electrodes do not require prior separation of the NPs and ions and measure the decrease in absorption or increase in free ions in solution, respectively.

Finally, because an important part of these NP dissolution studies is determining the effect of key NP parameters on dissolution, comprehensive NP characterization (e.g. NP size and shape dispersity or surface chemistry) plays an important role in determining the effect of each NP parameter as well as on extracting trends between studies.[174] This comprehensive characterization is not always achieved; however, where possible, we use characterization data provided in the studies to draw conclusions about how NP parameters impact dissolution.

3.1 AgNPs: Mechanisms of Ion Release

For bulk Ag, the dominant scale product under ambient conditions is Ag_2S. For AgNPs, Ag_2S forms during exposure to gaseous H_2S or Na_2S or in wastewater treatment plant conditions.[175-180] Since Ag_2S has an extremely low K_{sp} ($6\text{x}10^{-51}$),[36] it can protect the interior Ag from further oxidation and dissolution, and ion release from particles with surfaces composed of Ag_2S is much lower compared to un-sulfidized AgNPs.[175, 181-184] Although aggregation can sometimes occur in these conditions, forming chain-like structures of Ag_2S,[183] other studies in which the AgNPs are adsorbed to a substrate (and are thus not aggregated) show that the decrease in Ag(I) ion release is due to sulfidation and not aggregation.[175]

In more simple solutions, it has been shown that ion release from AgNPs occurs only in the presence of oxygen,[185-187] suggesting that oxidation of the AgNP surface is a limiting step in the ion release process. The most commonly proposed oxidation product, Ag_2O, has been characterized on AgNP surfaces by changes in the AgNP localized surface plasmon resonance (LSPR) peak,[188-192] by X-ray diffraction (XRD)[191] and X-ray photoelectron spectroscopy (XPS).[193]

For the formation of bulk Ag_2O, $\Delta G_f^o = -11.25$ kJ/mol at 298 K.[103] However, Zhang has proposed that the free energy of Ag_2O is radius-dependent according to the following equation:[193]

$$\Delta G_f^o = -11.25 - 57.5/r$$

where r is the NP radius in nm, and the value 57.5 comes from the free energy due to particle curvature.

In addition, the redox potential of AgNPs may decrease with size (*vide supra*). The redox potential of bulk Ag is 0.799 V vs. SHE,[103] but at the lower limit of one Ag atom, Henglein has demonstrated that the redox potential can decrease to -1.8 V.[163]

Once Ag_2O is formed, it can then dissolve in the presence of protons (Figure 2A) according to the following reaction:[187, 194]

$$Ag_2O + 2H^+ \rightarrow 2Ag^+ + H_2O$$

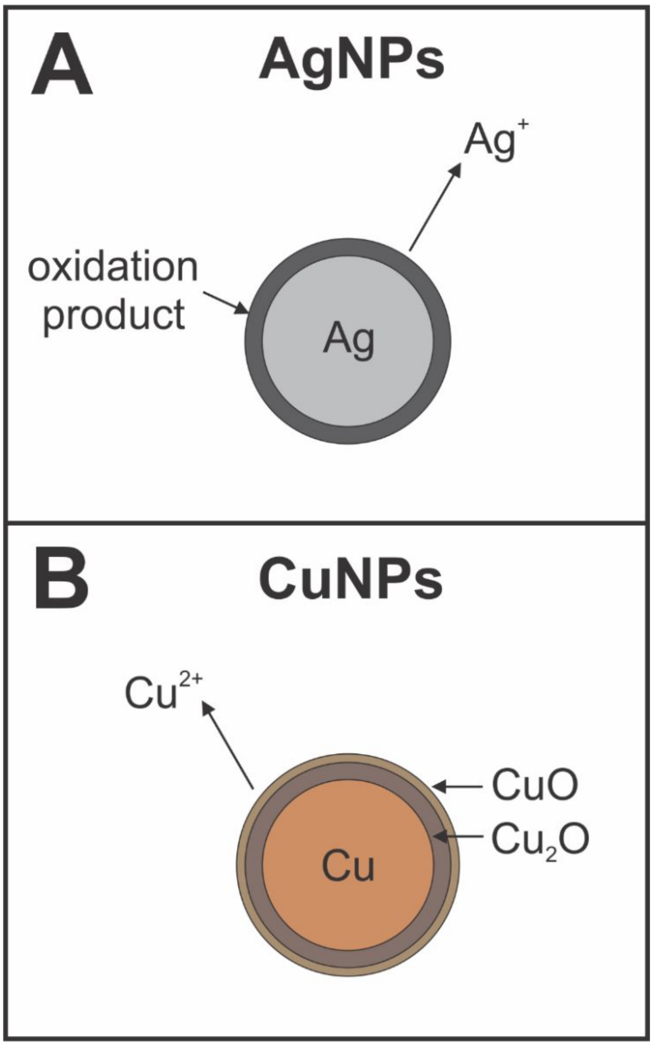

Figure 2. Summary of the most prevalent deterioration processes that occur for AgNPs and CuNPs (not to scale).

The ΔG^o for this reaction in the bulk is -71.8 kJ/mol,[194] making the overall oxidation/dissolution reaction of Ag thermodynamically favourable (ΔG_f^o = -83.1 kJ/mol).[187] However, complete AgNP dissolution is not normally observed in Ag(I) ion release studies.[185, 195, 196] Indeed, for AgNPs with diameters larger than 8 nm, the concentration of released Ag(I) ions has been shown to correspond to approximately 1 ML of dissolved Ag_2O, while for AgNPs with diameters less than 5 nm, the concentration of released Ag(I) ions corresponds to approximately 2 MLs of dissolved Ag_2O.[195] This incomplete dissolution behaviour could be due to kinetics, which could limit dissolution due to factors such as NP stabilization by ligands or particle aggregation. Another possible explanation for the incomplete dissolution behaviour of AgNPs is that the dissolution could reach some equilibrium state if the volume of the medium is limited (i.e., if the medium is not flowing over the AgNPs or is not continually replaced over the course of the experiment). However, Hiemstra suggests that the incomplete dissolution of AgNPs is due to the formation and dissolution of a different oxidation product according to the following reactions:

$$Ag_3OH + O_2 + 3H^+ \leftrightarrow 3Ag^+ + 2H_2O + O^\bullet$$
$$Ag_6 + O^\bullet \leftrightarrow Ag_6O$$

where Ag_3OH is the proposed oxidation species of Ag (where each Ag has +1/3 charge), Ag_6 is the underlying metallic lattice, and Ag_6O stabilizes the particle surface so that Ag release stops before full dissolution.[196, 197]

It is still unclear which of the above proposed AgNP oxidation products form in solution. In both cases, it is agreed that the AgNP surface is at least partially oxidized, leading to dissolution into Ag(I) ions in the presence of protons. This dissolution and the factors that control it are the focus of many studies, and we will begin by reviewing the work that has been done to determine how the intrinsic properties of AgNPs contribute to Ag(I) ion release.

3.1.1 AgNP Size. The effect of size on the dissolution of AgNPs is well-studied. As discussed above, the small size of AgNPs leads to a larger percentage of surface atoms compared to bulk Ag. In addition, the small size of AgNPs leads to a greater thermodynamic driving force towards oxidation of the AgNP surface, which can lead to greater dissolution.

It is sometimes difficult to separate the effect of size from the effect of other AgNP properties (e.g., to obtain various sizes of AgNPs, different ligands might be required, which results in changing more than one variable at a time). Here, we only discuss the effects of AgNP size on Ag(I) ion release when the other AgNP properties (surface chemistry and shape) remain constant. Results from these types of studies show that smaller AgNPs release more Ag(I) ions or have a higher rate of Ag(I) ion release,[160, 184, 186, 195, 197-211] which is consistent with the Ostwald-Freundlich equation (*vide supra*). Although a few studies claim that larger AgNPs release more Ag(I) ions or release ions at a faster rate,[208, 212] this could be due to the limited size range or time period studied.

However, determining trends based on diameter alone may not represent the true picture of Ag(I) ion release. For a given material mass and shape, the NP diameter will determine the surface area exposed to solution. Using the data provided in the papers discussed, we correlated the reported Ag(I) ion release values with the total surface area of AgNPs exposed to the solution (Table S1). Some studies show the expected result that a larger exposed surface area results in greater Ag(I) ion release.[160, 195, 197, 198, 201, 202, 208] However, other studies show that a smaller exposed surface area results in greater Ag(I) ion release,[184, 186, 198-202, 204, 206-209] which is not an intuitive result and confirms that there are other factors in addition to the exposed surface area that affect Ag(I) ion release.

3.1.2 AgNP Surface Chemistry. As discussed above for AgNP size, it is sometimes difficult to compare the effect that different ligand chemistries have on Ag(I) ion release even within the same study, since changing the ligand chemistry can also change other NP properties, such as size. In all cases here, we compare surface chemistry-dependent ion release only when the AgNP sizes are similar. The vast majority of the current literature reports Ag(I) ion release based on ligand *identity*, although there are other ligand parameters of interest such as ligand *arrangement* and ligand *density* that may also contribute to observed dissolution behaviours.

It is interesting to first compare Ag(I) ion release from “bare” AgNPs (i.e. NPs with no intentionally-added ligands, although ions or solvent molecules are most likely present on the NP surface) to ion release from AgNPs that have intentionally-added organic molecule ligands on their surface. As discussed above, the primary role of ligands is to provide stability, so bare AgNPs are not as stable as AgNPs with intentionally-added ligands. As a result, the bare AgNPs can aggregate, which increases their effective size and decreases the amount of Ag(I) ions that are released compared to more stable AgNPs that have organic molecule ligands adsorbed.[160, 206, 213, 214] On the other hand, if the bare AgNPs were not aggregated, one might expect them to release more ions than AgNPs with organic molecule ligands, due to the greater accessibility of the surface to oxygen. Indeed, bare AgNPs adsorbed to a substrate (thus not aggregated) have a higher rate of dissolution than AgNPs with ligands.[215]

Two of the most common organic molecule ligands for AgNPs are citrate and polyvinylpyrrolidone (PVP). Ag(I) ion release from each of these particle types has been well-studied, although the results are conflicting. In some cases, Ag(I) ion release from citrate-AgNPs is greater.[206, 209, 216-218] The most likely explanation for this behaviour is that PVP is a bulky polymeric ligand that can passivate the AgNP surface more efficiently than citrate so that there is less accessibility to oxygen. However, in other cases, Ag(I) ion release from PVP-AgNPs is greater.[202, 208, 209, 217, 219-221] The two most common explanations for this behaviour are: 1) the PVP-AgNPs are more stable against aggregation or 2) citrate can re-reduce Ag(I) ions or chelate released Ag(I) with its unbound carboxylate group, which would keep the Ag(I) ions associated with the AgNPs during analysis.

A third category of AgNPs is those that are functionalized with thiol ligands, which have a relatively strong (~20-25 kcal/mol)[222] interaction with the AgNP surface. In most cases, the presence of thiol ligands (such as 11-mercaptoundecanoic acid or thiolated poly(ethylene glycol)) results in lower Ag(I) ion release due to their strong interaction with the AgNP surface which can protect it from oxygen.[184, 223, 224]

3.1.3 AgNP Shape. Just as it is difficult to differentiate the effects of size on Ag(I) ion release from those of surface chemistry and vice versa (*vide supra*), it is also difficult to differentiate the effects of shape on Ag(I) ion release from those of surface chemistry and size. The syntheses of different NP shapes may require the use of different ligands, and the surface area exposed to solution for the different NP shapes may differ. For example, although Ag prisms have been found to release less Ag(I) ions than pseudospherical AgNPs,[225] the prisms in this study were functionalized by both citrate and PVP, as opposed to the functionalization of the pseudospherical NPs by PVP only. In another study, it was found that the specific surface area of various NP shapes correlates with Ag(I) ion release,[226] but it would also be useful to study these shapes while keeping the specific surface area constant to isolate the effect of shape.

3.2 Cu and CuO NPs: Mechanisms of Ion Release

For Ag, most ion release studies discussed above indicate that particles are synthesized with metallic Ag surfaces, that then may oxidize over time to form some type of Ag oxide. For Cu, characterization methods such as XPS and/or XRD demonstrate that the surface of CuNPs is also at least partially oxidized in the presence of oxygen.[227-243] Indeed, the surface of CuNPs is shown by multiple studies to be composed of mostly Cu_2O with a thin layer of CuO on top (Figure 2B), similar to the products observed for oxidation of bulk Cu.[228, 229, 232-234, 237, 238, 243] The surface of these oxidized CuNPs is similar to the surface of as-synthesized CuO NPs, so we also include CuO NPs in our discussion of Cu ion release.

3.2.1 Cu and CuO NP Size. Compared to AgNPs, there are fewer studies examining the role of Cu/CuO NP size on ion release, although we would expect that Cu and CuO NPs would follow the same thermodynamic principles as discussed above. Consistent with this prediction, the studies that do report ion release from CuO NPs of various sizes find that the smallest NPs release the most ions.[244, 245] However, the expected trend, where as size increases, ion release decreases is not necessarily followed.[245]

Relative to the small number of studies that determine ion release for multiple sizes of NPs, there is a much larger set of literature in which ion release from micro or bulk CuO is compared to ion release from CuO NPs. As expected, these studies overwhelmingly find that CuO NPs release more ions than micro or bulk CuO.[227-230, 246-258]

In most of these studies of size effects on ion release from CuO NPs, aggregation is a significant concern. Many size studies report aggregation of CuO NPs,[227-229, 244-255] which could be due to either insufficient surface stabilization, since most do not report the presence of intentionally-added ligands (*vide infra*), or the properties of the medium in which the CuO NPs are dispersed. Aggregation changes the effective size of the NPs (and therefore the exposed surface area per unit mass), which can impact the conclusions in studies which report ion release from various sizes of CuO NPs.

3.2.2 Cu and CuO NP Surface Chemistry. The effect of surface chemistry on ion release from Cu and CuO NPs is relatively less understood than it is for AgNPs. In fact, most studies claim that their Cu or CuO NPs are “bare,” which leads to rather polydisperse particles. In one such study, bare CuO NPs release more Cu ions than thiolated CuNPs.[259] Other studies have compared bare CuO NPs to carbon-coated CuNPs and again find that the bare CuO NPs release more ions.[253, 260] Tween 80 has also been shown to decrease dissolution.[243]

Similar to AgNPs, sulfidation has been shown to affect ion release from CuO NPs. In one case, sulfidized CuO NPs release less Cu ions than unsulfidized CuO NPs,[261] which is consistent with the results for AgNPs. However, in another case, sulfidized CuO NPs release more Cu ions than unsulfidized CuO NPs.[262] This conflicting result was explained by the possible existence of small metal sulphide clusters that could pass through the filter during the experiment.

3.2.3 Cu and CuO NP Shape. Ion release from CuO spheres has been shown to be higher than ion release from CuO rods.[257] In the study, the two different shapes had approximately the same surface area, so the difference in ion release is attributed to the higher potential of the rods to aggregate, which results in lower ion release.

3.3 AuNPs

Bulk Au has been shown to be inert in both ambient and high temperature conditions (*vide supra*). AuNPs are somewhat less inert, and AuNPs (especially those with diameters below 5 nm) have been shown to be active catalysts for reactions such as the oxidation of carbon monoxide.[263, 264] However, we could not identify any current reports showing AuNPs that undergo oxidation and ion release processes similar to AgNPs and CuNPs.[265, 266]

4. Deterioration of NPs via Environmental Factors

Just as the environment affects the deterioration of bulk metals, it will also contribute to the deterioration of metal NPs and affect their desired function. There are a variety of environments to which NPs are likely to be exposed, beginning when they are synthesized, continuing while they are used in an intended application, and ultimately through to the end of their life (potentially including unintentional environmental release).

The environmental factors that have been studied for NP dissolution include: pH, chloride concentration/ionic strength, temperature, light, and the presence of additional molecules in the solution (including both small molecules and NOM). Many of the experiments that will be discussed here choose laboratory solution conditions that mimic real world scenarios (e.g. a particular concentration of chloride at a particular pH to mimic relevant conditions such as a nutrient growth broth or water found in the environment). Other studies measure ion release in various “real world” media such as microorganism growth media,[182, 199, 200, 204, 206, 209, 214, 223, 227-229, 237, 238, 244-252, 254, 255, 258, 261, 267-287] physiological fluids,[203, 234, 252, 256, 288-292] or environmental media.[182, 187, 199, 202, 208, 212, 213, 217, 220, 223, 224, 239, 240, 242, 253, 293-303] These studies do not often make explicit connections between the chemistry of the environment and the ion release profile but do make connections between the identity of the media and the observed ion release profiles.

The studies on ion release as a function of environment (along with the studies on ion release as a function of intrinsic NP properties, discussed in Section 3) have two broad purposes: 1) to determine how intrinsic and environmental factors affect the antimicrobial activity of the NPs and the mechanism of that antimicrobial activity (i.e., whether the released ions, the NPs themselves, or both are important for antimicrobial action) and 2) to determine the fate of NPs in an accidental environmental release scenario. Not every study that will be discussed in the following sections explicitly relates ion release to antimicrobial activity or environmental fate, and it is beyond the scope of this review to discuss these relationships in detail. However, in general, studies of NP dissolution have allowed us to determine that antimicrobial activity is not solely induced by released ions via a chemical mechanism but rather is induced in synergy with the physical action of the NPs themselves.[304] There is also NP-specific activity that can occur independently from released ions or in their absence (e.g., when other ions and organic compounds complex with the released ions, hindering their bioavailability and mitigating their antimicrobial activity), although the relative contributions of each component towards antimicrobial activity is determined by the environment. The exact particle-specific mechanisms and the order and timescale of reactions that occur within the cell-NP system remain unresolved. For more on this topic, we refer the reader to previous reviews that discuss the toxicology of various forms of Ag[174, 305, 306] and we have also conducted a recent study on the relative contributions of AgNPs and Ag(I) ions to antimicrobial activity.[304]

4.1 AgNPs

The solution conditions that affect Ag(I) ion release from AgNPs have been studied extensively and reveal the behaviour of AgNPs in a wide variety of environments.

4.1.1 Effect of pH. Not surprisingly, pH has been shown to contribute to Ag(I) ion release from AgNPs. As can be seen in the above proposed dissolution reaction equations, protons can drive the dissolution of AgNPs. As a result, when the pH of the solution is lowered, Ag(I) ion release increases.[187, 197, 198, 203, 225, 270, 307-309] There have been some studies which show the opposite or no trend,[205, 271, 293] but in one case H_2O_2 was used as the oxidant instead of O_2,[205] and in the other cases aggregation may have obscured correlations with pH.[271, 293]

4.1.2 Effect of Chloride Concentration and Ionic Strength. The presence of chloride or other ions in solution can impact the speciation of the Ag(I) ions that are released from AgNPs. Specifically, for chloride, the extent of AgNP dissolution is dependent on the formation of various possible silver chloride species, which is dependent on the Cl:Ag ratio. As the Cl:Ag ratio increases, soluble $AgCl_x^{(x-1)-}$ species dominate over AgCl(s).[310] Conditions which favour the formation of $AgCl_x^{(x-1)-}$ complexes (i.e. solutions with a high Cl:Ag ratio) lead to greater AgNP dissolution compared to water, due to the high solubility of those complexes.[218, 220, 273, 310, 311] On the other hand, conditions which favour the formation of AgCl(s) (i.e. solutions with a low Cl:Ag ratio) lead to less AgNP dissolution compared to water.[182, 185, 310, 311] Overall, we can arrange the conditions in order of increasing AgNP dissolution: small Cl:Ag ratio, pure water, high Cl:Ag ratio.

Although chloride has been the most studied, the effect of other ions, including nitrate and phosphate ions, has also been studied. Of course, increasing ionic strength, regardless of ion identity, can increase the extent of AgNP aggregation via the reduction of inter-particle electrostatic repulsion. If the NPs are aggregated, the extent of ion release per particle will decrease.[312, 313] However, in at least one case, authors have determined that chloride concentration is more important than ionic strength in determining Ag(I) ion release (where chloride ions were compared to nitrate and phosphate analogues), and therefore also a more important factor than NP aggregation state in determining total released Ag(I) ions.[312]

4.1.3 Effect of Light. Two studies have examined the effect of light on Ag(I) ion release, and the results show that the reactive oxygen species generated during light exposure influence Ag(I) ion release. When AgNPs are exposed to wavelengths of light that overlap with the AgNP localized surface plasmon resonance, $O_2^{\bullet-}$ forms, which can re-reduce released Ag(I) ions and thus decrease Ag(I) ion release.[311] However, the opposite has also been reported where light exposure enhances Ag(I) ion release even though $O_2^{\bullet-}$ forms.[221]

Of course, the light sensitivity of silver halides is well known, and has been exploited for over a century in photography.[314, 315] Therefore, there is reason to expect that there will be effects of light on the stability of oxidized silver surfaces, especially those that contain silver halide scales and/or are releasing Ag(I) complexed to chloride or other halides. However, to date, we have not found reports studying these effects explicitly in terms of Ag(I) ion release from NPs.

4.1.4 Effect of Temperature. The effect of temperature on Ag(I) ion release has not been studied extensively, but AgNPs released into the environment or used in antimicrobial applications are likely to be exposed to a variety of temperatures. In the studies reported, Arrhenius behaviour is generally observed, where the extent of ion release increases as temperature increases.[187, 219, 273]

4.1.5 Effect of Additional Dissolved Matter in Solution. Of particular importance for AgNPs released into the environment or in biological media are the other molecules present in solution. It is extremely rare, outside of a controlled laboratory experiment, for AgNPs and their ligands to be the only components present in the solution. Thus, there has been a significant effort to determine how dissolved matter influences Ag(I) ion release. The most common ways in which these molecules are postulated to affect ion release are by passivating the NP surface (and thereby lowering the ion release) or by chelating released Ag(I) ions (and driving more Ag(I) ions into solution, via a Le Chatelier-type process).

In experiments where known quantities of small molecules (e.g. cysteine, glutathione) are introduced to an aqueous suspension of AgNPs,[184, 185, 267, 272, 293, 313, 316-320] there are conflicting results concerning the effect of these molecules on Ag(I) ion release. Some studies have shown that these molecules increase Ag(I) ion release.[267, 272, 313, 316] The proposed mechanism for this enhancement is that the molecules can bind released Ag(I) ions, driving more Ag(I) ions into solution. However, other studies have shown that these molecules decrease Ag(I) ion release.[184, 185, 293, 317-320] In some cases, this apparent decrease in ion release may instead be a retention of high molecular weight Ag(I)-cysteine species centrifugal filters, and therefore only a sub-set of Ag(I) species are detected.[317] In other cases, the decrease of Ag(I) ion release as a function of small molecule introduction has been attributed to binding of the small molecules to the AgNP surface, which could decrease Ag(I) ion release, possibly by inhibiting oxygen interaction with the surface.

Interestingly, the literature does not suggest a correlation between small molecule:Ag mole ratio and the inhibition or enhancement of ion release (Table S2; i.e. low small molecule:Ag mole ratios do not always lead to increased Ag(I) ion release/binding of Ag(I) ions and high small molecule:Ag mole ratios do not always lead to decreased Ag(I) ion release/interaction with the AgNP surface). This lack of concentration dependence would seem to indicate that perhaps the proposed mechanisms are not mutually exclusive, and both may be occurring simultaneously, leading to an unclear concentration dependence.

In addition to any small molecules present in real world solutions, more complex species, generally called NOM, can also be present. In the Ag(I) ion release experiments discussed here, NOM is most commonly composed of humic or fulvic acids. As with the small molecules, increasing concentrations of NOM have been shown to both increase[318, 321-323] and decrease[187, 216, 224, 293, 319, 322, 324] Ag(I) ion release, and the most common explanations are again that the NOM binds released Ag(I) ions or binds to the AgNP surface, respectively. For NOM, there also does not appear to be a definitive correlation between low NOM:Ag mole ratio leading to increased Ag(I) ion release and a high NOM:Ag mole ratio leading to decreased Ag(I) ion release. However, in general, in the majority of studies in which NOM is reported to decrease Ag(I) ion release, there is a relatively high NOM:Ag mole ratio (Table S3), which may suggest that the dominant mechanism in these cases is that the NOM binds to the NP surface and prevents ion release either by steric, chelating, or chemical stabilization (e.g. protection from oxidation).

4.2 Cu and CuO NPs

The solution conditions that affect ion release from Cu and CuO NPs have been relatively less studied than those for AgNPs. Nevertheless, we discuss the relevant literature and attempt to elucidate general trends. In many cases, the trends for AgNPs and CuNPs and/or CuO NPs are similar.

4.2.1 Effect of pH. As can be predicted from the bulk Cu dissolution reaction shown above, as the pH of the solution decreases, the ion release from Cu or CuO NPs increases, and this has been consistently observed for all Cu NPs and CuO NPs studied.[231-234, 253, 255, 260, 261, 290]

4.2.2 Effect of Chloride Concentration and Ionic Strength. Conflicting results have been found for the effect of chloride on ion release from Cu or CuO NPs. In some cases, when chloride is present, ion release from Cu or CuO NPs decreases.[233, 246, 301] However, another study finds that as the concentration of chloride increases, the ion release from CuO NPs increases, but there is no clear trend for ion release from CuNPs.[231] These differences may be due to the formation of CuCl(s) in the cases where ion release decreases or soluble complexes such as $CuCl_2^-$ in the cases where ion release increases, similar to the discussion above for the deterioration of bulk Cu in the presence of chloride.

Just as with most of the other environmental factors, ionic strength has been less studied for Cu and CuO NPs than for AgNPs. However, increasing ionic strength (with phosphate buffer) has been shown to increase ion release.[233]

4.2.3 Effect of Light. Light has not yet been shown to impact ion release from CuO NPs.[325]

4.2.4 Effect of Temperature. Similar to AgNPs, ion release from Cu and CuO NPs follows Arrhenius behaviour under the conditions studied thus far, where increased temperature leads to increased ion release.[302]

4.2.5 Effect of Additional Dissolved Matter in Solution. Similar to AgNPs, NOM has been shown to either increase or decrease ion release from Cu and CuO NPs. In the studies where NOM is shown to increase the release of Cu ions, it is generally hypothesized that the NOM complexes the released Cu ions, thus driving more ions into solution.[231, 233, 300, 303] On the other hand, when NOM is shown to decrease the release of Cu ions, it is generally hypothesized that the NOM coats the NP surfaces, protecting them from dissolution.[231, 242]

5. Outlook and Challenges

The release of metal ions from NPs has far-reaching implications. For example, applications such as catalysis and bioimaging require NPs that resist deterioration in order to retain the desirable features of the original NP. Conversely, in applications such as antimicrobials, the rate and extent of ion release is critical to NP performance. Therefore, understanding and leveraging dissolution from NPs such as AgNPs and CuNPs, which undergo oxidative ion release, is crucial. The size, shape, and surface chemistry of the NPs are all useful handles for dissolution control, but their interplay is yet to be fully described or leveraged. Downstream environmental factors of the NP exposure then either enhance or inhibit the intrinsic particle deterioration processes.

The works summarized here show the progress that has been made in studying, controlling, and leveraging ion release from metal NPs. However, some challenges remain. A first major challenge is identifying the oxidation products that lead to ion release, which may be different from the oxidation products observed in the bulk. This is most problematic for Ag, where: 1) Ag_2S is the major product of deterioration in the bulk, even at minority concentrations of sulphur-containing species. Yet, at the nanoscale, both Ag_2S and Ag oxides have been observed in different conditions, and interestingly, the majority of work on NPs suggests that a Ag oxide surface has formed. While we discuss potential driving forces for this difference in scale product formation (e.g. changes in apparent surface reduction potential, and differences in equilibria established under various aqueous conditions, Section 3.1), such a large discrepancy in material outcomes is worthy of further research effort. 2) If we assume that Ag oxides form, there is still not agreement on the specific identity of those species. 3) The frequent presence of halides in downstream environmental/biological exposures of AgNPs complicates the possible observed surface compositions significantly, and the surface chemistry of AgNPs may approach the diversity more commonly associated with bulk Cu surfaces.

In addition to the chemical diversity observed during nanoscale metal deterioration processes, there are analytical challenges associated with monitoring the extent and pathway(s) of these reactions. For example, some of the methods used to determine the extent of metal ion release require separating reaction solutions from the original NPs before quantification (e.g. ICP-MS/OES, GF-AAS). The separation step can introduce errors if there are species that are either included or excluded during purification. On the other hand, methods such as ion-selective electrodes may inadvertently only measure certain forms of the dissolved ions.[322] In addition, bulk ion release measurements determine the total metal ion concentration in solution and do not necessarily reflect the quantity of ions that organisms may be challenged with locally. Therefore, intracellular measurement methods are also desirable complements to bulk solution analysis.

Analysis of the NP itself before, during, and after exposures to the environment can also be challenging. Quantitative assessment of ligand populations, as well as chemo-specific analysis of the inorganic core, all require bulk measurements using current analytical methods. New methodologies will need to be developed to assess particle-to-particle variations in environmental impact and to ultimately establish a comprehensive understanding of NP deterioration mechanisms and impacts.

Finally, the factors that contribute to metal NP ion release are often inter-related. For example, changing one NP or environmental factor may result in a change to another factor (e.g. changing NP surface chemistry may change the NP size, or changing the media may change emergent NP surface chemistry). NP morphology can also change over the course of the experiments. For example, the NP size may decrease as dissolution occurs, the shape may change to lower NP surface energy, and the surface chemistry may change due to solution conditions. These changes can lead to uncertainty in the effects of intrinsic NP factors on ion release.

Overcoming these obstacles first requires an appreciation for, and the patience to study, the rich and potentially powerful chemistry that arises in these commonly studied systems. Then, the daunting analytical challenge of measuring and monitoring the complex interplay between chemical reactions that occur between a NP and its environment must be tackled. Yet, taken together, the promise of coinage metal NPs and the potential value of their size-dependent chemical reactivity is strong motivation to meet these challenges.

Conflicts of interest

There are no conflicts to declare.

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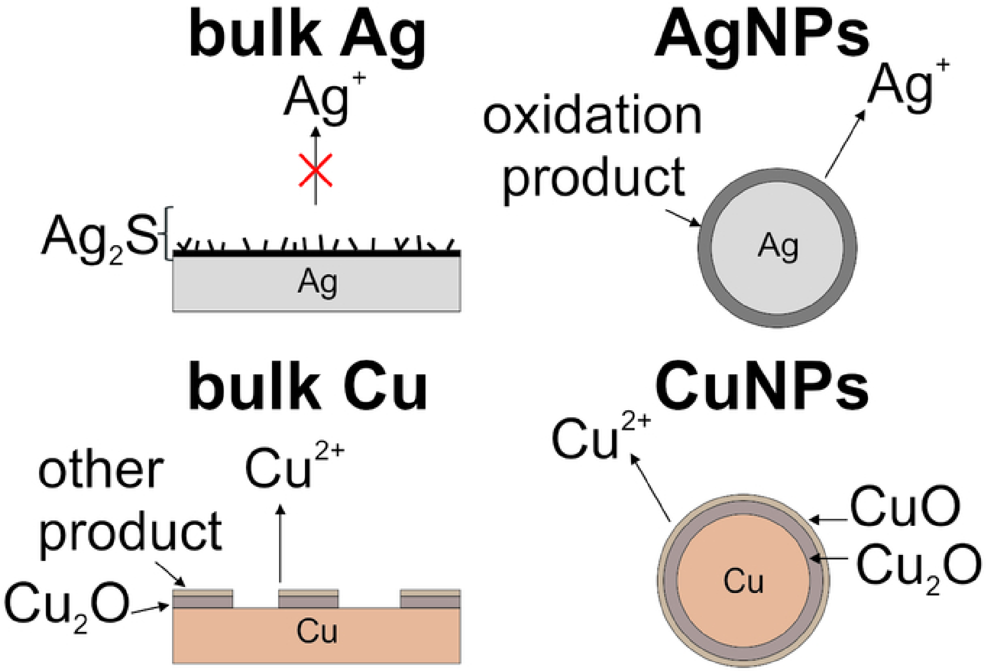

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