Review of oxidative dissolution and sulfidation of select nanoparticles in the environment: Impact on applications

Tana L. O'Keefe,[†] *Christy L. Haynes*[†]*

[†] Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455, United States

*Corresponding author: chaynes@umn.edu

ABSTRACT.

Nanoparticles (NPs) are increasingly being used in medical, electronic, energy, and agricultural applications due to their unique properties that often arise due to the high surface area-to-volume ratio. However, this characteristic along with the high reactivity of NPs make these materials highly dynamic in environmental settings. Thus, several transformations can take place when these materials enter the environment that determine the transport, toxicity, and fate of these materials in our environment. These transformations, and more specifically oxidative dissolution and sulfidation, are directly impacted by the characteristics a NP has in addition to the environmental conditions. Therefore, this review aims to summarize how NP characteristics (size, coatings, etc.) and other important environmentally relevant conditions (oxic/anoxic, natural organic matter, etc.) impact oxidative dissolution and sulfidation of several metal and metal oxide NPs. The impact of these factors is crucial in understanding and predicting the environmental risks of these materials in a wide range of applications.

Keywords: Engineered nanoparticles, environmental transformations, dissolution, sulfidation, size, coatings, natural organic matter

1. Introduction

Engineered nanoparticles (NPs) have become integral components in various industrial, biomedical, and consumer applications due to their unique physicochemical properties. Their small size often creates high surface area-to-volume ratios that result in novel properties and high reactivities. For example, silver is typically inert but when scaled down to produce Ag NPs, it becomes catalytic[1] or can have antimicrobial properties.[2-4] However, these high reactivities make NPs highly dynamic when they enter the environment, either intentionally through agricultural applications or unintentionally through improper disposal of products or devices containing NPs. Within the environment, a NP may be exposed to oxygenated or deoxygenated water sources, natural organic matter (NOM), biological organisms, and other macromolecules that can impact their transformations. Additionally, many NP syntheses can easily be tuned to alter their size, shape, and surface coating for various applications, but this adds further complexity when trying to understand and predict the transport, toxicity, and fate of these materials in our environment. As the use of NPs continues to expand, there is a clear need to fully understand how a NPs' characteristics and the surrounding conditions in the environment impacts their transformations.

Several transformations, including oxidation-reduction (redox) reactions, dissolution, aggregation, sedimentation, sulfidation, reactive oxygen species (ROS) generation and redox reactions can take place when NPs interact with the environment.[5] Specifically, the oxidative dissolution and sulfidation processes emerge as critical mechanisms that can govern the transformation and transport of these NPs in the environment. Oxidative dissolution, involving the release of metal ions through an oxidation reaction, and sulfidation, characterized by the formation of metal sulfide species, are two pivotal pathways that determine the speciation and bioavailability of NPs and their released ions in the environment. These two transformations are directly impacted by a NP's characteristics and the surrounding environmental conditions, so this review will investigate how these factors impact a limited set of NPs that include metal (Ag NPs) and metal oxide (CeO_2, CuO, and ZnO) and Cd-based quantum dots (QDs).

Several industries have incorporated QDs and metal and metal oxide NPs into an extensive range of products and applications (Figure 1). It is challenging to estimate the use of NPs in consumer products as not all products that contain NPs are clearly identified; however, some have estimated that 260,000-309,000 metric tons of NPs were produced globally in 2010, and the worldwide consumption of NPs expected to soar to 585,000 metric tons by 2020.[6] Additionally, the global market for nanotechnology is expected to increase from approximately $68 billion in 2023 to $183 billion by 2028.[7] The majority of NPs utilized in consumer products are metal and metal oxide NPs. Metallic NPs, such as Ag NPs, are extensively used for their antimicrobial properties in wound dressings,[2] drug delivery,[8, 9] textiles including clothing,[3, 10, 11] and food packaging.[4, 12] They also differ from their bulk counterpart which is largely inert as Ag NPs have high reactivities and have been used for the catalytic synthesis of organic compounds[1] in addition to the degradation of pollutants in water.[13] Additionally, Ag NPs have been incorporated into photovoltaics to enhance the efficiency of solar cells by improving light absorption and electron transport.[14, 15] Metal oxide NPs, including CeO_2, CuO, and ZnO NPs, are also commonly used in biomedical, electronic, energy, and agricultural applications due to changes in their electronic and optical properties. Ceria or CeO_2 NPs are found in catalytic converters,[16] and batteries,[17, 18] and they have been used in photocatalytic water splitting to generate hydrogen as a clean and sustainable fuel.[19] Additionally, they have been incorporated into gas sensors that allow for the detection of carbon monoxide, nitrogen dioxide, and arsenate ions[20, 21] and biosensors that detect gas markers in human breath to provide a disease diagnosis.[22] Similar to Ag NPs, CuO NPs are incorporated into biomedical applications for their antimicrobial properties[23, 24] and can catalyze the decomposition of organic pollutants in wastewater.[25-27] They have also found use as gas sensors to detect nitric oxide[28] and hydrogen sulfide[29] and have been explored in agricultural applications since they

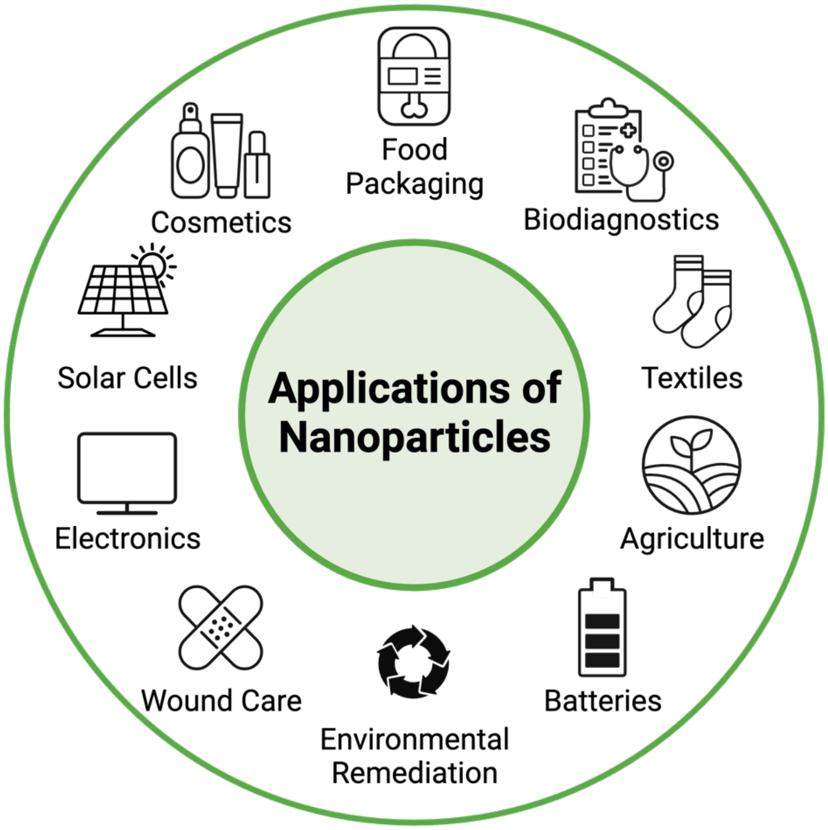

Figure 1. Applications of nanoparticles. Figure created with BioRender.com

can serve as nanofertilizers or nanopesticides due to their fungicidal and bactericidal properties.[30, 31] ZnO NPs are most known for their presence in sunscreens and other cosmetics as they effectively block ultraviolet light waves.[32-34] Other common uses of ZnO NPs include the degradation of synthetic dyes in water,[35] removal of heavy metals such as lead and chromium from water,[36, 37] and incorporation into dye-sensitized solar cells for improved solar cell efficiency.[38, 39] They have also been effective as nanofertilizers that promote plant growth and mitigate plant stress at low concentrations, although excessive application can lead to toxic effects on the plant and have negative consequences on the surrounding soil microbial communities.[40, 41] Lastly, inorganic NPs, such as CdSe QDs, are popular in consumer products because of their tunable emission wavelength, high quantum yields, and greater photostability when compared to traditional organic dye molecules. For these reasons, QDs are often present in LED displays,[42-44] and they have been utilized for *in* vivo and *in* vitro biological imaging.[45-47] As another application, Cd-based QDs have been incorporated into biosensors that can detect mutation changes within DNA fragments for lung cancer diagnosis [42] or for the detection of microRNAs that serve as cancer biomarkers for ovarian and prostate cancer.[48] It is evident from the examples above that there is a wide range of applications for these NPs with some intentionally being applied in the environment (agricultural applications) while other NPs can unintentionally enter the environment (washing off textiles, improper disposal, etc.); however, much still remains unknown about how these NPs transform within our environment once they have completed their life cycle as a consumer-use item. Therefore, this review paper aims to provide an overview of the various factors that impact oxidative dissolution and sulfidation of metal (Ag), inorganic (Cd-based quantum dots), and metal oxide (CeO_2, CuO, ZnO) NPs to better understand these transformations in our environment. Factors that will be discussed include NP size, oxidation state, and surface coatings in addition to light intensity, oxic/anoxic conditions and the impact of NOM.

2. Chemical Oxidation and Reduction

One way that oxidation-reduction reactions with nanoparticles can occur is through chemical transformations of the nanoparticle chemical structure. This involves the transfer of electrons to and from chemical moieties that are part of the nanoparticle itself and its environment. Several nanoparticles (NPs) including silver, transition metal oxides, and QDs contain elements that can readily undergo oxidation or reduction reactions in various environments. Typical oxidizing systems include oxygen-rich environments such as natural waters and aerated soils, whereas reduction often occurs in oxygen-depleted environments including groundwater depleted of oxygen and carbon-rich sediments. In dynamic environments, NPs experience cycling of oxidation-reduction reactions and may be found to contain different oxidation states.[5] Factors that influence oxidation-reduction reactions and the rate at which they occur include: size, surface area, surface modifications, oxidation state of the elements that make up the NP, and environmental conditions such as oxygen levels, pH, and media components. Several of these factors for specific nanomaterials will be discussed below.

2.1 The Effect of Size

It is generally assumed that oxidative dissolution increases as particle size decreases and the nanoparticle presents a higher relative surface area. In fact, solubility is a function of nanoparticle size, and a modified version of the Kelvin equation, known as the Ostwald-Freundlich relation, can be used to relate NP solubility to its radius (eq 1).

$$S_r = S_{bulk} \times \exp(2\gamma V_m / RT \times r) \qquad (1)$$

Where S_r is the solubility of the NP with radius r, S_{bulk} is the solubility of the nanoparticle material in bulk with a flat surface, γ is the surface tension of the particle (J/m^2), V_m is the molar volume of the particle (m^3/mol), R is the gas constant, and T is temperature in Kelvin.[49] However, it can be challenging to observe this size effect on its own as many synthesized NPs have surface modifications. One study measured the dissolution of 5-80 nm Ag NPs coated with organic polymer coatings including poly(vinylpyrrolidone) (PVP) and gum arabic.[49] The results revealed that smaller Ag NPs have faster oxidative dissolution in sodium bicarbonate solution, and this extent of dissolution was attributed to the size of the NPs rather than other factors, such as coating type or synthesis method. This size effect, where Ag NPs experience more dissolution at smaller sizes, has also been observed for citrate-coated Ag NPs in environmentally relevant buffers[50-52] and natural waters[53] in addition to Ag NPs in neutral and acidic conditions.[54] Beyond Ag NPs, size-dependent dissolution has been reported for ZnO NPs[55, 56] and CeO_2 NPs.[57] In one study, the 4 nm ZnO NPs showed greater oxidative dissolution than the 15 nm and 240 nm NPs.[56] In the CeO_2 NP study, all of the tested CeO_2 NPs underwent oxidative dissolution to release Ce^{3+}, with the smallest (~9 nm) NPs releasing twice as many Ce^{3+} ions as the two larger (~23 and 64 nm) NPs. While bulk ceria and large ceria NPs are mainly in the Ce(VI) oxidation state, small ceria NPs take on the Ce(III) oxidation state to release lattice strain.[58] It has been shown that the lattice strain increases exponentially for CeO_2 NPs when they are below 25 nm, resulting in an increase of Ce(III) on the NP surface that can lead to an increase in dissolution.[57, 58] In this study, it was evident that the smaller CeO_2 NPs contain more soluble Ce^{3+} (~23%) on their surface compared to the other two particles (~10 and 11%) with the remainder of the NPs consisting of Ce(IV). While this could be a size effect that is observed, the oxidation state of the oxide also plays a critical role in CeO_2 NP oxidative dissolution.[57]

2.2 The Role of Oxidation States of Metal Oxides

Cerium dioxide (CeO_2, or ceria) NPs are commonly used to investigate the role of oxidation state in NP oxidative dissolution. As mentioned above, the Ce(III) oxidation state is more prevalent in smaller CeO_2 NPs due to an increase in oxygen vacancies which helps to reduce lattice strain. Additionally, CeO_2 NPs have the ability to cycle between the Ce(III) and Ce(IV) oxidation states.[59] It is known that Ce(III) is relatively soluble ($Ce(III)(OH)_3$ $K_{sp} = 1.6 \times 10^{-20}$) while Ce(IV) is generally assumed to be insoluble ($Ce(IV)(OH)_4$ $K_{sp} = 2 \times 10^{-48}$).[60] In the environment, Ce^{3+} can readily dissolve from a CeO_2 NP surface, and newly exposed Ce^{4+} must undergo further reduction to Ce^{3+} before being released.

The oxidation state of Ce within CeO_2 NPs heavily depends on oxygen levels and the pH in the surrounding media.[61] In one study, smaller CeO_2 NPs which contained higher amounts of Ce^{3+} resulted in higher dissolution rates, and further reduction of Ce^{4+} to Ce^{3+} in acidic media resulted in higher release of Ce from the NPs due to proton-promoted dissolution.[57] These results agree with previous work that observed greater solubility for Ce^{3+} oxides at low pH when compared to solubilities observed for Ce^{4+} oxides (Figure 2).[60, 62, 63] pH is a critical factor when considering oxidative dissolution of NPs as it can dictate the oxidation state and the resulting oxidative dissolution. In fact, several studies have investigated the impact of low pH on the oxidative dissolution of Ag NPs[51, 64] and CeO_2 NPs.[61, 65, 66] Due to the various relevant compartments and the pH ranges that NPs can experience in the environment, pH should strongly be considered and covered more extensively in future work that explores the oxidative dissolution of NPs.

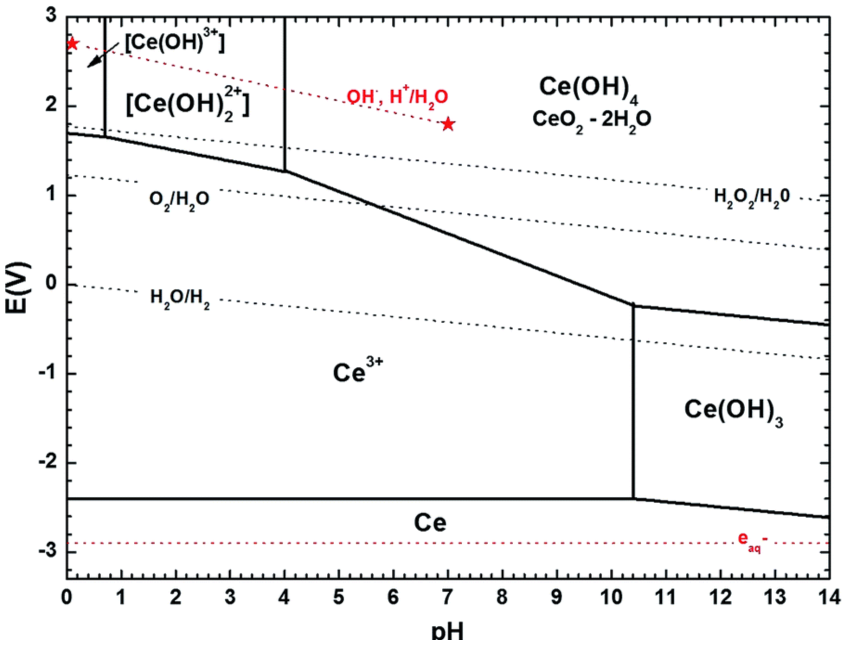

Figure 2. description here Revised version of a cerium Pourbaix diagram using more recent thermodynamic data on cerium species and computed here for a concentration of soluble Ce species of 0.1 mM. The pH-dependent redox potential or different redox couples associated to water, i.e. O_2/H_2O, H_2O_2/H_2O, H_2O/H_2 (dark dotted lines) and to radiolytic processes in water, i.e. (OH^-, H^+)/H_2O, aqueous electrons (red dotted lines) are also represented. Reproduced with permission from Ref 63. Copyright 2017 Royal Society of Chemistry.

Copper NPs also commonly include Cu in varying oxidation states: Cu^0, Cu^{1+}, and Cu^{2+}. It has been shown that in hydroponic media, nanoscale Cu, primarily in the zerovalent state, was quickly oxidized to release copper ions while dissolution was slower for nanoscale CuO and $Cu(OH)_2$ that contained Cu^{2+} and Cu^{1+}, respectively.[67] Copper ions are well-known to be toxic to several organisms; thus, slower dissolution may reduce the amount of free copper ions in solution, thereby reducing the hazards of these NPs in the environment. Although the effect of oxidation state on the dissolution of CeO_2 and Cu NPs has been studied in various pH and phosphate solutions that mimic groundwater and soil systems, there is still a need for further studies in more environmentally relevant conditions including natural and waste waters and soils where natural organic matter (NOM) is present as higher concentrations of NOM have the ability to bind to the NP surface, slowing NP dissolution and making them less reactive in the environment. NOM interactions will be further discussed in section 2.5.

2.3 Oxic vs Anoxic Conditions

Metallic NPs (Ag, Cu, etc.) are known to react with oxygen, either atmospheric or dissolved oxygen in water, to form metal oxides at their surface. These oxide layers result in faster dissolution of these materials in water, and if oxygen or other oxidizing agents are present, oxidation of the NP-exposed surfaces continues. Thus, oxygen plays a large role in the transformations of NPs in either oxygen-rich (natural waters) or oxygen-depleted (deep groundwater) environments.

A study performed on citrate-coated Ag NPs in both natural (oxygen-saturated) and deoxygenated waters demonstrated that removing dissolved oxygen from the water completely inhibited the release of Ag^+ ions, showcasing the essential role of O_2 in initiating surface oxidation of Ag NPs (Figure 3).[68] Similar results that showed inhibition of Ag^+ release were obtained for the dissolution of Ag NPs coated with amorphous carbon under anoxic conditions.[69] In another study, citrate-coated AgNPs showed lower dissolution to Ag^+ in anoxic conditions compared to oxic conditions.[70] Dissolution was further reduced in both oxic and anoxic conditions in the presence of natural organic matter (NOM).[70] The impact of NOM on dissolution will be further discussed in section 2.5. The lack of dissolved oxygen in water has also been observed to inhibit the dissolution of copper and titania NPs.[71]

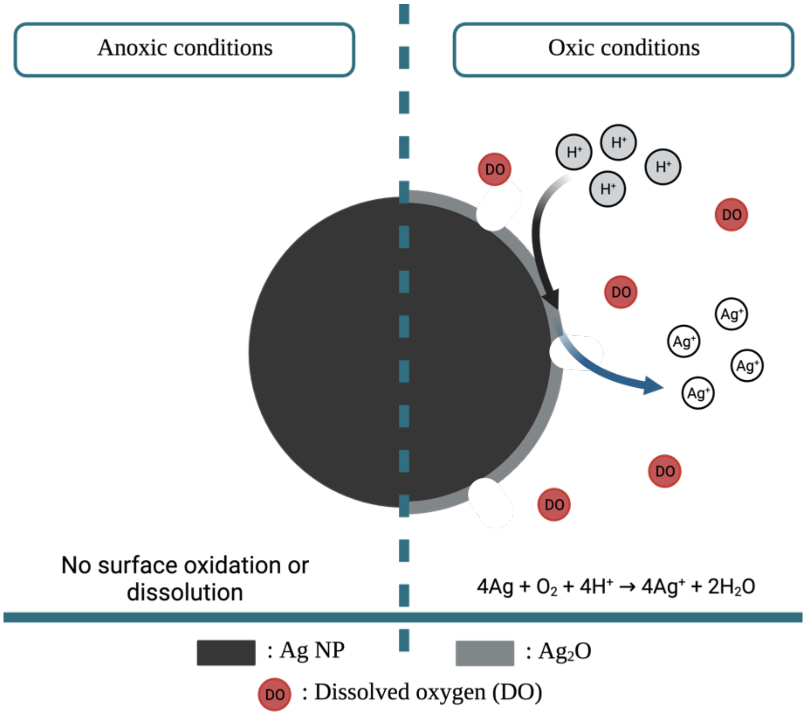

Figure 3. Schematic for the oxidative dissolution of Ag NPs in anoxic and oxic conditions. Figure created with BioRender.com.

Oxygen-limited environments appear to enhance the stability of NPs, resulting in less surface oxidation and release of ions that can be toxic (e.g., Ag^+) to other systems or undergo other transformations in the surrounding environment. While it may seem beneficial to have less oxidative dissolution of these NPs in oxygen-depleted environments, increasing the colloidal stability of the NPs in the environment still poses serious environmental risks as they can persist for longer periods of time and be subject to other transformations, including aggregation, sulfidation, and interactions with biomolecules or ROS.[72-74]

2.4 Role of Surface Coatings

Various coatings have commonly been used to stabilize NP dispersions, reduce NP toxicity, and decrease nonspecific interactions or promote specific interactions with cells or proteins;[75-80] however, NP coatings strongly influence dissolution as they initially act as physical barriers towards their environment.[81] The impact surface coatings have on dissolution is largely dependent on the type of surface coating and the means by which it is attached to the NP's surface.[82, 83] Some coatings have the ability to coordinate with surface atoms, while others are simply deposited and do not coordinate with surface atoms, but both typically block reactants from reaching surface sites on the NP and can slow reaction rates.[50] On the other hand, organic molecules can bind to metal surfaces through nucleophilic functional groups that may accelerate oxidation and dissolution.[52, 84]

Surface coatings have been widely explored for Ag NPs to limit their dissolution and toxicity. Typically, Ag NP coatings consist of organic acids (citrate, tannic acid), polymer coatings (PVP, PEG), or other macromolecules (chitosan, gelatin, etc.). Two of the most extensively studied coatings for Ag NPs are citrate and polyvinylpyrrolidone (PVP). Studies indicate that PVP-coated Ag NPs have a higher rate and final degree of dissolution when compared to citrate-coated Ag NPs.[85-87] It has also been observed that citrate coating leads to a lower Ag^+ release compared to tannic acid-coated,[53] gelatin-coated,[78] and chitosan-coated Ag NPs.[78]

Citrate coatings are known to act as electrostatic stabilizers since they modify the Ag NPs with negative charges to aid in their dispersity; however, it has been suggested these coatings also act as reducing agents, reducing the outer oxide layer that forms on the Ag NP back to zero-valent Ag, and thereby decreasing the NP's solubility.[88] It has also been hypothesized that the citrate coating acts as a chemical barrier because it can reduce outgoing silver ions.[85] One study suggests that the carboxylic groups on citrate act as an Ag^+ sink by binding released Ag^+ and decreasing the NP's solubility.[68] These studies are supported by evidence that the citrate ions on the Ag NP surface orient such that one terminal and the tertiary carboxylate groups of citrate complex to the silver surface while the second terminal carboxylate remains unbound, available to complex with released Ag^+.[89] In a similar manner to citrate binding released Ag^+, other polymer coatings such as polyacrylamide, poly(acrylic acid), and gum arabic have been observed to serve as Ag^+ sinks by complexing with released Ag^+.[50] However, bound Ag^+ is able to undergo reversible adsorption-desorption, altering the release profile of toxic Ag^+. Therefore, it is possible that these Ag^+ sinks can both delay and extend ion release by accumulating and later releasing stored inventories of bound Ag^+, where the dynamics are determined by the molecular character of the coating.[50] Additionally, dissolution is often initiated by chemisorption of oxygen; however, coating molecules including citrate, Na_2S, and 11-mercaptoundecanoic acid occupy these initial chemisorption sites limiting access to the surface and ultimately decreasing dissolution.[50]

In another study poly(ethylene glycol) (PEG) and a model protein, bovine serum albumin (BSA), were investigated as Ag NP coatings. PEG-thiols covalently attach to the Ag NP through the terminal thiol group so that the long PEG chain extends away from the NP surface, creating a self-assembled monolayer.[90] This creates a steric barrier restricting reagents from the Ag NP surface, resulting in minimal dissolution and almost no Ag^+ release.[81] On the other hand, BSA is not expected to strongly interact with the Ag NP surface, leaving the NP less protected and allowing for faster dissolution. In fact, BSA initially enhanced dissolution of the Ag NPs due to the dissolution of regions of the Ag NP that were not directly functionalized by BSA, but then BSA appeared to provide better protection against dissolution over extended periods of time.[81] This was supported by another study that observed an increase in Ag NP dissolution in the presence of BSA.[91] As somewhat expected, thicker protective layers with more Ag NP coverage serve as better coatings. Thus, surfactants have also been investigated as surface coatings.

One study suggests that Ag NP dissolution might be inhibited by surfactant coatings, including with the nonionic surfactant Tween® and the anionic surfactant sodium dodecyl sulfate.[88] However, in river water and upon exposure to sunlight, Tween®-coated Ag NPs released Ag^+ at a faster rate than citrate-coated Ag NPs,[92] highlighting the importance of studying several experimental conditions. Although the conclusions in these two studies are contradicting, it is apparent from both studies that the Tween coating increases stability, reducing aggregation of the Ag NPs. This results in greater mobility of the NPs in the environment that could potentially present a greater risk to organisms. Additional studies are necessary to fully understand the impact of these surface coatings under various environmental conditions.

It is evident that coatings can improve stability/dispersity while potentially slowing down dissolution and release of Ag^+. However, long term studies on the effect of surface coatings are lacking. It is possible that coatings may have little influence on the long-term behavior and solubility of the NPs since the coatings may detach from the NP surface or degrade over time.[93] Upon exposure to the environment, surface coatings on NPs also have the potential to be displaced or covered by natural biomolecules to form coronas,[94, 95] further complicating their environmental transformations.

2.5 Natural Organic Matter and Small Organic Acids

Natural organic matter (NOM) is a heterogeneous mixture of organic materials that is ubiquitous in surface waters and groundwater. NOM primarily consists of humic and fulvic acids with molecular weights ranging from ~1-5 kDa[96] and are typically enriched in carboxyl and phenolic groups.[97] NOM can play complex roles in NP transformation and can facilitate surface-mediated processes that alter nanoparticle stability, dispersion, and dissolution. For example, humic and fulvic acids bind to Ag NPs, which can inhibit dissolution by excluding oxygen that is needed to initiate Ag^+ release.[68, 98-100] Additionally, humic and fulvic acids can facilitate a cycle of oxidation and reduction for Ag NPs where new Ag NPs are formed by released Ag^+.[99, 101-105] Isotopic labeling studies demonstrated that dissolved $^{109}Ag^+$ concentration was rapidly decreased by Suwannee River humic acids, while the oxidation of ^{107}AgNPs to release $^{107}Ag^+$ was suppressed.[104] Understanding the role of NOM in NP transformations is further complicated due to a wide variation in composition for different natural sources.[106]

A comparison of humic and fulvic acids from different NOM sources demonstrated that Ag^+ release from Ag NPs stabilized with Pony Lake fulvic acid was lower than Ag NPs stabilized with Suwannee River humic acids, Suwannee River fulvic acids, and pristine Ag NPs.[86] The difference was attributed to high sulfur and nitrogen content for Pony Lake fulvic acids, which may suppress Ag NP dissolution due to enrichment of functional groups that complex with Ag^+, such as thiol groups, thiolates, and amines.[86] The reduction of Ag^+ by NOM suggests toxicity might be mitigated; however, the stabilizing effect of NOM has the potential to disperse Ag NPs in the environment over a long period of time and move them far from their original location. Thus, there is potential for Ag NPs to act as a sink for Ag^+ that may continue to cause persistent and harmful effects over time.

Contrary to Ag NPs, ZnO NP dissolution is enhanced in the presence of NOM. A comparison of NOM from 16 different sources demonstrated that the dissolution rate for ZnO NPs positively correlates with NOM aromatic carbon content and molecular weight, and negatively correlates with NOM aliphatic carbon content.[106] These trends were explained by an increased binding affinity between the Zn surface and NOM with increased molecular weights. Similar results with increased dissolution rates for ZnO were observed for strong chelating agents ethylenediaminetetraacetic acid (EDTA) and L-cysteine.[107] These NOM studies demonstrate that affinity of organic substances such as NOM for ZnO NPs is an important factor for understanding dissolution rates.

Similar to ZnO NPs, increased dissolution rates of CuO NPs have been observed in the presence of humic substances (Figure 4).[108-110] One study performed on CuO NPs suggests that interactions between the carboxylate groups on humic acid and the oxidized Cu surface create an adsorbed NOM layer that enhances dissolution.[110] Adsorbed humic acid polarizes the surface and destabilizes the metal-ligand complexes by weakening or breaking metal-oxygen or metal-metal bonds.[56] Sodium alginate and the protein bovine serum albumin also slowed dissolution, but not to the extent of humic and fulvic acids that contain higher amounts of functional groups and facilitate contact with the NP surface.[109] Additionally, increased dissolution rates of CuO NPs by small organic acids, including dihydroxy benzoic acid, citric acid, and oxalic acid, have been reported.[110, 111] Again, coordination of these organic acids weakens the metal-oxygen bonds on the oxidized surface, increasing Cu^{2+} release. This effect of organic acids on dissolution has also been observed for CeO_2 NPs with citric acid and ascorbic acid generating and releasing more Ce^{3+} ions.[112] The adsorption of NOM or small organic acids and the consequent dissolution of these NPs, increases

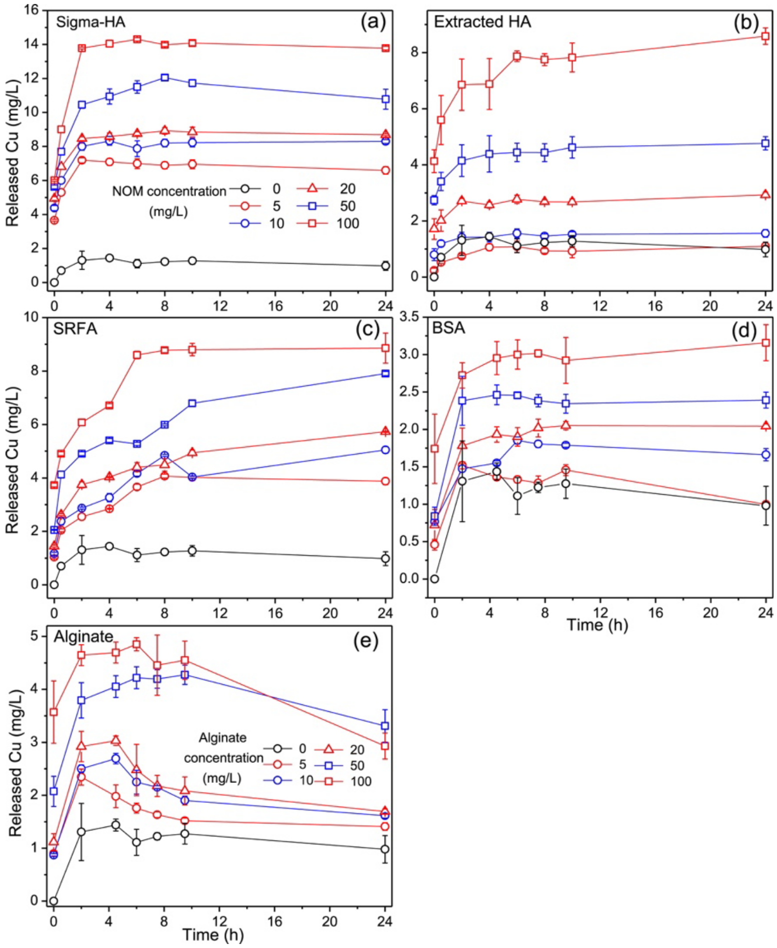

Figure 4. Copper release kinetics of CuO NPs at different NOM concentrations for a) Simga-humic acid, b) Extracted humic acid, c) Suwannee River fulvic acid, d) bovine serum albumin and e) alginate. The release of Cu increases with increasing NOM concentration. The error bars represent the deviation of duplicate samples. Reproduced with permission from Ref 109. Copyright 2015 Elsevier.

released metal ion concentrations while producing smaller NPs that have greater mobility. This has the potential to increase toxic metal ion bioavailability in the environment.

Overall, it is challenging to make general conclusions about the effect of NOM with such a wide variety of NOM molecules and NPs being investigated. Furthermore, NOM is rarely characterized at the molecular level in most studies, and the mechanisms wherein dissolution is enhanced or suppressed are not fully understood. These mechanisms, in addition to the full characterization of NOM and the long-term implications of organic matter on NPs, should continue to be explored. Looking at individual components of NOM to more fully understand the mechanisms that are driving oxidative dissolution rates should be investigated. Additionally, collaborations between environmental chemists and engineers to develop new methods to analyze these complex matrices should be a priority. Lastly, NOM is known to serve as a photosensitizer and produce ROS.[113] This can be beneficial for the degradation of organic pollutants or inactivation of microorganisms in water sources,[113] but ROS significantly alters the transformations of NPs in the environment, which also needs further investigation.

3. Photo Oxidation and Dissolution

Photo-oxidation is an oxidation reaction that occurs in the presence of light, and it is a crucial step in the environmental transformations of QDs. Similar to above, the environmental conditions and characteristics of QDs play a major role in the photo-oxidation and dissolution of QDs. Specifically, when CdSe QDs are excited by incident photons with higher energies than their band gap, a bound electron-hole pair is formed, which can then react with surrounding oxygen-containing molecules to produce reactive oxygen species (ROS), including O_2^-.[114, 115] Previous ROS scavenger experiments suggest that the produced O_2^- acts as a precursor and induces oxidative dissolution of the QDs.[116] This section will briefly cover the photo-oxidation of common QDs.

3.1 Light Intensity

Light intensity varies in natural water and saltwater systems and can impact the production of O_2^- and the resulting oxidative dissolution of QDs. One study focused on the dissolution of CdSe QDs with and without a ZnS shell in saltwater using natural light with varying UV intensities to replicate different sea depths.[117, 118] Furthermore, this study estimated that it could take over 2 years for QDs to settle into deeper water where dark conditions dominate and dissolution is minimal.[117] The aggregation of QDs and the various factors that impact this, such as high ionic strength of seawater, have been previously reviewed elsewhere.[119-121] However, colloidally stable QDs have sufficient time exposed to sunlight in the water column prior to settling to cause toxicity to organisms via dissolution of the CdSe QDs. In another study, aqueous suspensions of polymer-coated CdSe/ZnS QDs were studied under UV (254 nm) irradiation.[116] The dissolution to both Cd^{2+} and Se^{2-} ions was observed to significantly increase as the irradiation intensity increased, with slight dissolution still occurring under dark conditions. Additionally, equilibrium for the release of Cd was reached after approximately 5 hours of UV exposure whereas the equilibrium time for Se dissolution was approximately 12 hours. This suggests that there are other limiting factors for the photo-oxidation for these polymer-coated CdSe/ZnS QDs. Overall, these results suggest that photo-oxidation, that is dependent on the irradiation intensity experienced at various depths, contributes to photo-oxidation and dissolution of QDs.

3.2 Surface Coatings

Polymers are commonly used for QD coatings as they serve as reducing and stabilizing agents that minimize oxidation and agglomeration of QDs. It has previously been reported that QDs will be more photochemically stable if they are coated with longer chain, higher molecular weight, and structurally complex ligands.[122] In one study, the photo-oxidation and dissolution of CdSe/ZnS core/shell QDs with three different types of polymer coatings (polydiallydimethylammonium chloride (PDDA), poly(ethylene glycol) (PEG) with a carboxylic acid terminal end group, and PEG with an amine terminal end group were investigated.[116] Dissolution to Cd^{2+} was the highest for PEG-carboxylic acid-coated QDs, followed by PEG-amine-coated QDs and then the PDDA-coated QDs. The results agree with previous findings as the PDDA polymer has a longer chain length and is structurally more complex than PEG.[122] Although none of the coatings prevented photo-oxidation, they slightly inhibited oxidative dissolution by 4-20%, which is also consistent with previous studies on CdSe QDs,[123] CdSe/ZnS QDs,[124] CdTe QDs,[125] and thiol-capped CdTe QDs.[115]

It has also been shown that coatings or capping agents such as ZnS on CdSe QDs help mitigate QD toxicity.[123] One study explored the dissolution of CdSe QDs, CdSe/ZnS QDs with PDDA, and CdSe/ZnS QDs with carboxylic acid;[117] the authors found that the Cd^{2+} dissolution rate for the CdSe QDs with no ZnS shell was higher than both QD samples with the ZnS shell. While the mechanism remains unknown, this suggests that the ZnS shell plays a crucial role in preventing the QDs from undergoing oxidative dissolution, with the shell potentially serving as a barrier that limits the exposure of the CdSe QD core to the oxidative species formed upon photoexcitation.[117]

3.3 Oxic and Anoxic Conditions

Similar to chemical redox reactions, the photo-induced oxidative dissolution of QDs is suppressed when dissolved oxygen is absent. PDDA-coated CdSe/ZnS QDs underwent UV (254 nm) irradiation and greater dissolution of Cd^{2+} and Se^{2-} was observed under oxic conditions when compared to anoxic conditions.[116] Furthermore, it was evident that the Cd^{2+} and Se^{2-} concentrations in deoxygenated solutions plateaued, indicating that oxidative dissolution was not sustained after the depletion of residual dissolved oxygen.[116] This slowed dissolution and inhibition of Cd^{2+} release upon the removal of oxygen has similarly been observed for CdTe QDs,[125] CdSe QDs,[123] and mercaptopropionic acid-capped CdSe/ZnS QDs.[126] These results suggest that preventing exposure of QDs to oxidative environments could inhibit their dissolution and release of toxic Cd^{2+} and Se^{2-}. However, the presence or absence of oxygen not only impacts the oxidative dissolution of NPs, but it can also lead to the formation of ROS that has implications in the transformation of NPs in the environment, which has been reviewed elsewhere.[127]

3.4 Impact of Natural Organic Matter

The effect of NOM on QD dissolution is strikingly different in the presence or absence of light. There have been no changes observed on the extent or rate of QD dissolution when exposed to NOM in the dark. Specifically, exposure of Suwannee river humic and fulvic acids to carboxylic PEG- and amine PEG-functionalized CdSe/ZnS QDs showed no release of Cd^{2+} ions.[128] Additionally, under limited light conditions, the presence of humic acid did not affect CdSe-COOH QD dissolution over a 30-day period,[117] and a 3-month study showed no lasting influence of Suwannee river NOM on the rate and extent of MPA-capped CdSe/ZnS QD dissolution.[126] However, in the presence of light when QD dissolution is favorable, humic acid has been shown to increase dissolution of QDs. One study detected a two-fold increase in PDDA-coated CdSe QD dissolution upon exposure to humic acid,[116] while another study observed an increase in the dissolution rate of CdSe-COOH QDs exposed to humic acid.[117] It is hypothesized that this increase in QD dissolution is caused by the generation of ROS by humic acid aided by the light exposure.[121, 129] With the strong dependence on the presence or absence of light, it is evident that overall light intensity and the generation of ROS are more important factors than the presence of NOM.

4. Sulfidation

Another transformation, sulfidation, is the process of sulfide ions adsorbing onto the surface of a material. Sulfidation has been suggested as a natural detoxification process for metallic nanomaterials due to the low solubilities of metal sulfides that often result in a decrease of metal bioavailabilities.[130-132] This process has been demonstrated to be important for Ag, ZnO and CuO NPs in the environment as it can alter their surface charge, potentially limit oxidative dissolution of the metal or metal oxide NPs, and thus change their bioavailability and toxicity.[130, 133, 134] Metal and metal oxide NPs may undergo sulfidation by reacting with sulfide in reducing environments such as wetlands, swamps, subaquatic sediments, and wastewater treatment plants. In subaquatic sediments, sulfide produced from microbial sulfate reduction is present at concentrations ranging from 1 to 100 μg/L,[135] while sulfide concentrations in wastewater treatment plants range from a few μg/L up to 10 mg/L.[131] Additionally, NPs that enter wastewater treatment plants and undergo sulfidation frequently end up in biosolids that are applied as fertilizer on croplands.[134] Sulfidation of NPs has the ability to alter NP reactivity, transport, and ecotoxicity within the environment; therefore, it is important to understand this sulfidation process.

4.1 Sulfidation of Silver NPs

Sulfidation has widely been studied for Ag NPs, and it is known that the extent of Ag NP sulfidation is dependent on the sulfur to Ag NP ratio, with increasing formation of Ag_2S observed as sulfur concentration increases.[130, 131] There are two main mechanisms for the sulfidation of Ag NPs: indirect and direct sulfidation (Figure 5). Indirect sulfidation of Ag NPs is expected to proceed via oxidative dissolution of Ag to Ag^+ followed by precipitation of Ag_2S secondary NPs while direct sulfidation involves the direct transformation of the Ag NP surface to

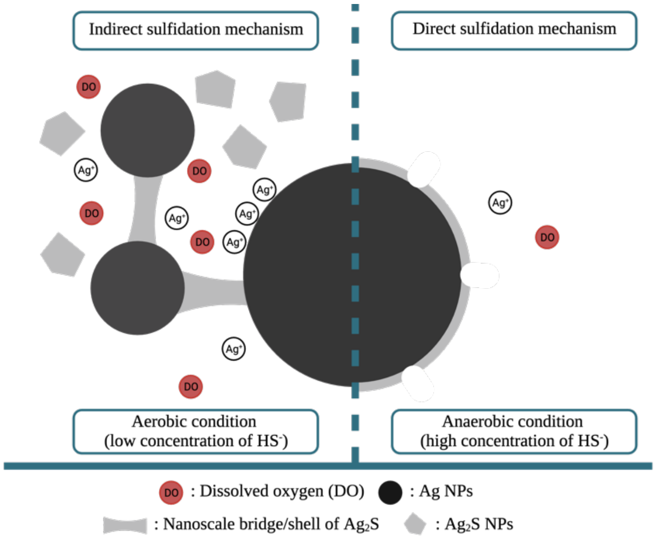

Figure 5. Scheme of the indirect (left) and direct (right) sulfidation mechanisms of Ag NPs. Figure created with Biorender.com.

Ag_2S.[131] Typically, at high sulfide concentrations (tens-hundreds mg/L), the direct oxysulfidation is preferred and produces an Ag_2S shell on the Ag NP with only small amounts of new smaller Ag_2S NPs being formed.[136] However, at environmentally relevant lower sulfide concentrations, the indirect sulfidation mechanism is favored where the NPs undergo oxidative dissolution, and released Ag^+ reprecipitates to form smaller Ag_2S NPs.

4.1.1 Direct Sulfidation

Direct sulfidation of Ag NPs has been observed in laboratory studies and at wastewater treatment plants under anoxic conditions.[137-139] In one study, silver nanowires (AgNWs) underwent direct oxysulfidation to produce Ag_2S NPs directly on the surface of the AgNWs.[137] Another study used Na_2S as a sulfide source and observed direct sulfidation even at low concentrations of sulfide (0.05 S/Ag molar ratio). Additionally, the formation of an insoluble Ag_2S layer on the surface of the metallic Ag core dramatically decreases the rate of dissolution for the Ag NPs.[139, 140] Direct sulfidation in low oxygen environments may be beneficial as the production of Ag_2S on the NP surface decreases dissolution and produces relatively insoluble NPs. Nonetheless, the largely insoluble Ag_2S NPs may act as Ag^+ sinks that could degrade or undergo other environmental transformations over time, releasing the stored Ag^+ from their core and causing adverse effects.

4.1.2 Indirect Sulfidation

Indirect sulfidation is likely to dominate in the environment due to the presence of oxygen and lower sulfide concentration. Thus, the indirect sulfidation mechanism has been observed for PVP-coated Ag NPs at low (10^{-3} M). sulfide concentrations. As a result of the simultaneous oxidation, that results in the release of Ag^+ and sulfidation of the Ag NPs, Ag_2S nanobridges formed between the NPs, leading to chain-like structures (Figure 6).[142]

As was observed for oxidative dissolution, the PVP capping agent did not protect the Ag NP from undergoing sulfidation. Furthermore, the formed Ag_2S NPs reduced their surface charge, making them relatively unstable and more likely to aggregate. However, indirect sulfidation still decreases the dissolution of Ag NPs as Ag_2S is highly insoluble ($K_{sp} = 8 \times 10^{-51}$). This decrease in dissolution has been shown to strongly limit the release of toxic Ag^+, decreasing its bioavailability and toxicity to several organisms including *Escherichia coli*,[3] *Caenorhabditis elegans*,[141, 143] Zebra fish embryos,[141] Killifish embryos,[141] and Duckweed.[141]

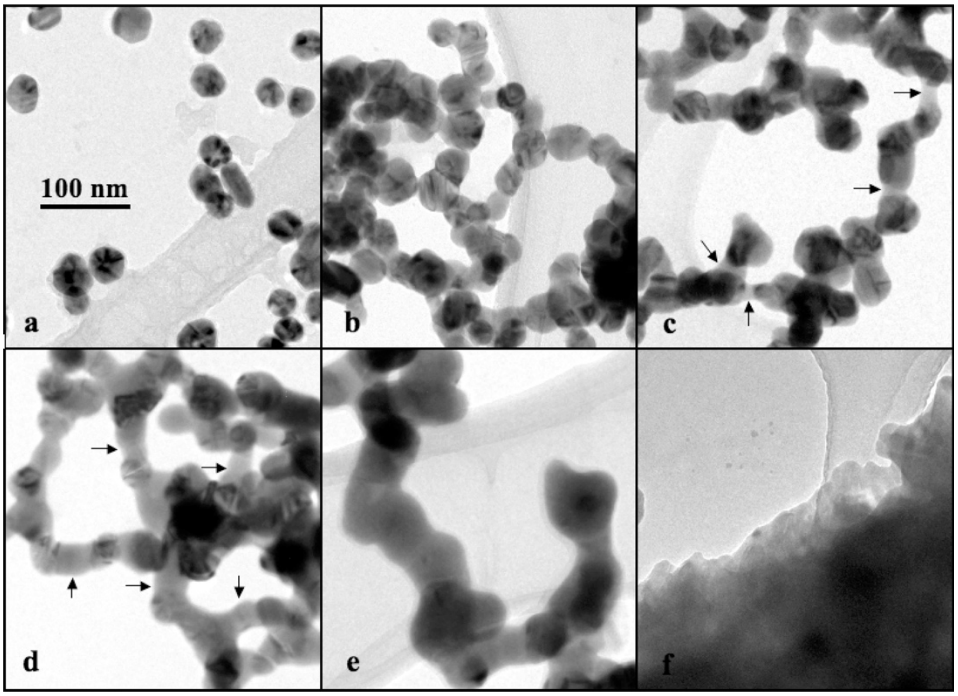

Figure 6. TEM images of the initial and sulfidized synthetic Ag NPs: (a) initial; (b) S/Ag = 0.019; (c) S/Ag = 0.055; (d) S/Ag = 0.308; (e) S/Ag = 0.540; (f) S/Ag=1.079. Magnification is identical for all six images. Reproduced with permission from Ref 142. Copyright 2013 American Chemical Society.

Sulfide sources in most laboratory studies use Na_2S, which differs from the sulfide sources found in the environment, H_2S and HS^-. While Na_2S is convenient for laboratory studies, the commercial purity is often poor and it can contain significant amounts of elemental sulfur and polysulfides that impact sulfidation studies. For example, several laboratory studies indicate almost complete sulfidation of Ag NPs over the course of hours to days,[144-146] but sulfidation in the natural environment occurs much slower.[136] An

18-month long-term sulfidation study performed on PVP-coated Ag NPs in a simulated wetland environment indicated incomplete sulfidation of the Ag NPs at the end of the study. Approximately 52% of the Ag NPs in terrestrial soils transformed to Ag_2S while approximately 55% and 27% of Ag NPs in subaquatic sediments were transformed to Ag_2S and Ag-sulfhydryl compounds, respectively. Additionally, it was observed that this partial sulfidation did not halt the release of toxic Ag^+, making it bioavailable to plants and other organisms.[141] The incomplete transformation of the Ag NPs to Ag_2S after 18 months, in addition to the release of Ag^+ suggests that the indirect sulfidation of Ag NPs in low oxygen natural environments occurs slower than has been observed in numerous lab studies. It is clear from this work that laboratory studies can provide predictions for the sulfidation process in the environment, but they do not fully capture the complexity of Ag NP sulfidation in a natural environment.

The impact of NOM on oxidative dissolution was outlined in section 2.5; similarly, interactions with NOM affect the extent or rate of sulfidation on Ag NPs, although the evidence for the effect of NOM on the sulfidation of Ag NPs is rather contradictory. Specifically, humic acid has been observed to increase the sulfidation of Ag NPs[131, 145] but suppress sulfidation in Ag NWs, suggesting this process is shape (or crystal face) dependent.[137] Previous studies have also reported that the adsorption of NOM could promote the stability of Ag NPs, and in turn, reduce aggregation and increase the surface area of the NP allowing for more interactions with sulfide ions.[145] Furthermore, it has been hypothesized that humic acid on the surface can serve as a transport channel and facilitate access to HS^- to the NP surface.[145] However, humic acid suppressed the sulfidation of Ag NWs, and this result is potentially explained by an increase in electrostatic repulsion between the negatively charged Ag NWs and sulfide ion in the presence of NOM.[137] Another type of NOM, Suwanee river fulvic acid suppressed sulfidation of Ag NPs.[139] Previous studies suggest Ag NPs have high affinity for fulvic acids due to their high sulfur and nitrogen content.[86, 147] Thus, fulvic acids potentially wrap the NPs, limiting their surface interactions and decreasing their oxidative dissolution. In turn, this decrease in oxidative dissolution results in suppressed sulfidation. Ultimately, the difference in experimental conditions between Ag NP and NOM sulfidation studies makes it challenging to draw any general conclusions from work published to date. In the future, more controlled studies with properly characterized NOM and full characterization of the NPs before and after sulfidation must be performed to make accurate predictions for these environmental interactions that dictate sulfidation.

4.2 Sulfidation of Ag NPs by Metal Sulfides

While it is common for sulfidation to occur in anoxic environments where the sulfide source is abundant, sulfidation has also been observed under oxic conditions. In the presence of oxygen, dissolved sulfide is readily oxidized;[148] however, considerable levels of dissolved copper and zinc ions in surface waters can potentially scavenge dissolved sulfide to form metal sulfides that are more resistant to oxidation.[149] Thus, metal sulfides (CuS and ZnS) may serve as a pool of sulfide in oxic zones of urban wastewater systems or in surface waters that may be available to react with Ag NPs.[150, 151] Therefore, studies have been performed to investigate the use of the metal sulfides CuS and ZnS to enable sulfidation of Ag NPs under oxic conditions.

In one such study, bulk CuS and ZnS both caused sulfidation of citrate-stabilized Ag NPs with the rate increasing with decreasing NP size and increasing metal sulfide concentration.[144] Sulfidation increasing with a decreasing NP size is similar to the trend observed for oxidative dissolution in section 2.1. Furthermore, as sulfidation increased, a decrease in the release of Ag^+ was observed in addition to an increase in dissolved Cu^{2+} and Zn^{2+}. The mechanism of sulfidation for Ag NPs by CuS NPs under oxic conditions was further investigated in another study that proposed the sulfidation reaction occurs through oxygen-dependent oxidative dissolution and release of Ag^+ followed by a cation exchange reaction between the silver ions and CuS NPs to form Ag_2S NPs.[152] A recent study confirmed this cation exchange reaction between Ag NPs and ZnS as well.[153]

Additionally, the sulfidation of Ag NPs by metal sulfides is suppressed in the presence of NOM and inorganic salts ($NaNO_3$, NaCl, $CaCl_2$).[152] As previously stated, the wrapping of NPs due to their high affinity towards NOM likely contributes to the decrease in Ag NP dissolution and sulfidation. As for interactions with inorganic salts, both NaCl and $CaCl_2$ showed stronger suppression of sulfidation compared to $NaNO_3$. This difference has been attributed to the formation of AgCl precipitates resulting from Ag^+ release and high levels of Cl^- in solution.[154]

4.3 Sulfidation of Metal Oxide NPs

In the presence of sulfide, the transformation of ZnO to ZnS occurs readily at ambient temperatures.[134] This relatively quick transformation to ZnS has previously been observed in wastewater treatment plant biosolids that did not involve the addition of ZnO NPs[155] along with biosolids that were amended with ZnO NPs.[156] The extent of ZnO sulfidation is dependent on the sulfide concentration, with the complete conversion of ZnO to ZnS NPs observed within approximately 5 days with sufficient addition of sulfide.[134] In this study, an inconsistent porous shell of newly formed ZnS NPs on the ZnO core was observed, suggesting that the sulfidation reaction occurs through the dissolution of Zn^{2+} and reprecipitation onto the ZnO surface. The ZnS shell promoted aggregation and combined with higher degrees of sulfidation, slowed the release of Zn^{2+}.[134] However, toxic Zn^{2+} was still readily released for NPs with lower degrees of sulfidation; thus, the potential for reducing toxicity and bioavailability may be limited until higher degrees of sulfidation of the ZnO NPs is attained.

Sea-urchin shaped ZnO nanospheres (NSs) have also been observed to undergo sulfidation to produce ZnS nanocrystals through the dissolution-reprecipitation mechanism.[157] NOM was found to suppress dissolution and sulfidation of the sea-urchin like ZnO NSs through the ligation of Zn^{2+} by NOM, which has previously been reported.[158] Furthermore, completely sulfidized sea-urchin shaped ZnO NSs showed minimal toxicity to *E. coli* since there was negligible release of Zn^{2+}.[157] More long-term studies are still needed as the small size of the newly formed ZnS NPs on the ZnO surface could be highly reactive in the environment, while larger agglomerates of ZnS NPs could also allow for slower transformations and an increase in other interactions in a complex environment.

Copper oxide (CuO) NPs also undergo sulfidation to produce CuS NPs in the presence of inorganic sulfide at ambient temperatures with the extent of sulfidation largely dependent on the sulfide to CuO molar concentration ratio.[133, 159, 160] The mechanism for sulfidation of CuO NPs occurs similarly to the dissolution and reprecipitation sulfidation mechanism of ZnO NPs as observed secondary CuS NPs were much smaller than the original CuO NPs (50 nm).[133, 159] While higher extents of sulfidation for Ag and ZnO NPs have been shown to decrease solubility and limit their release of toxic ions, sulfidation of CuO increased the amount of dissolved Cu^{2+} compared to pristine CuO NPs, regardless of the presence or absence of dissolved oxygen.[159, 160] In fact, the greater dissolution of CuS NPs and the resulting release of Cu^{2+} was found to be toxic to Japanese medaka, an aquatic organism that has the potential to be exposed to these sulfidized NPs.[160]

Furthermore, another study showed that CuS produced from the sulfidation of CuO NPs can act as a catalyst for sulfide oxidation. More specifically, CuS may be oxidized by ROS (e.g. H_2O_2) found in natural environments. The conversion to an oxidized sulfide species destabilizes the copper in the CuS lattice, leading to the release of toxic Cu^{2+} and solution-based Fenton activity.[133] Therefore, it is hypothesized that CuO sulfidation does not fully detoxify Cu in systems where ROS may be present.[133, 160] This observed catalytic activity is likely not only applicable to CuO NPs, but also likely relevant for nanocopper materials that undergo surface oxidation upon exposure to oxygen in the environment. Together, these findings suggest that sulfidation of CuO NPs may actually increase their apparent solubility and the resulting bioavailability and toxicity that is attributed to Cu^{2+}. Thus, it seems likely that sulfidation is not a natural antidote for all metallic NPs in the environment.

5. Outlook and conclusion

As the use and application of NPs continues to expand, there are some serious considerations that scientists should study, including performing life cycle analyses of these materials before commercialization of NP-containing products in addition to performing full characterization of NPs before and after oxidative dissolution or sulfidation processes to more fully understand these transformations. Furthermore, it could be beneficial for chemists to collaborate with environmental scientists to remove engineered NPs that already exist in our environment to gain insight into the long-term transformations of these materials. Currently, NP interactions and transformations within the environment are too complex for modeling experiments, but as modeling continues to develop, these transformations should be investigated. Even simple modeling experiments that look at interactions between a NP surface and smaller components or functional groups of NOM may provide useful insight on how to better study these interactions experimentally. Previously, thermodynamic modeling for complex metal oxides showed pH-dependent cation release trends.[161, 162] Similar models could be expanded upon for NPs discussed within this review to provide insight on the environmental fate and toxicity of these materials in the environment. Additionally, the development of a database that includes NP characteristics, environmental conditions studied, etc. would be helpful for researchers to observe trends and draw conclusions. This database could also serve as a method for predicting other NP interactions in the environment for new emerging materials that may have similar characteristics to ones already within the database. Currently, there is a large gap that exists between NP production and NP waste management as the small size of NPs makes disposal and recycling a major challenge.[163] Additionally, with a broad range of existing NPs, and it is likely that a single recycling or disposal method will not suffice. It is crucial for scientists and science policymakers to work together to develop and implement regulations and policies for proper methods that are easily accessible to collect and recycle or dispose of products that contain NPs to reduce the chance of them entering and creating negative impacts in our environment. Furthermore, to implement these regulations and policies, it is vital for scientists and policymakers to communicate these methods and opportunities to the general public.

From the discussion above, it is clear that oxidative dissolution and sulfidation transformations are affected by a NP's characteristics and the components present in the surrounding environment; however, much still remains unknown about the long term impact these materials may have upon their release into our environment. Several of the factors described within the review are dependent on NP composition while others have similar trends across several metal or metal oxide materials. In general, as the size of a NP decreases, the resulting oxidative dissolution increases. It is also observed that lower oxidation states (Ce(III) and Cu(0)) undergo slower dissolution. Oxygen is a critical component for the oxidative dissolution of metal and metal oxide NPs, and this process can be suppressed in the absence of oxygen. Surface coatings can add complexity to the NP system; however, it is generally true that thicker, more protective coatings slow dissolution, although few long-term studies have been performed to fully understand any long-term effects. The impact of NOM on oxidative dissolution of metal and metal oxide NPs has contradictory results depending on the type of NP and NOM studied. For QDs, we observe that light and oxygen are key factors in photooxidation and dissolution, and NOM also increases dissolution of these materials. While sulfidation has been suggested as a natural detoxification process for several metal and metal oxide NPs, there are other environmental factors such as NOM and ROS that complicate the sulfidation process, making the sulfidation detoxification process less useful for some metallic NPs such as copper-based NPs. Understanding NP oxidative dissolution and sulfidation transformations allows us to further study the biological and ecological impacts. With this information, we can better predict the environmental risk of NPs and how best to mitigate the risks that emerge so that we can safely make use of NPs in a range of application areas.

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Conflicts of interests

No interests are declared.

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