CRITICAL REVIEW

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Silver sulfide nanoparticles in aqueous environments: formation, transformation and toxicity†

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Sulfidation of silver nanoparticles (Ag-NPs) readily occurs in both urban sewage systems and sulfur-rich natural environments with formation of silver sulfide nanoparticles (Ag$_2$S-NPs). It is essential to understand the transformation and fate of Ag$_2$S-NPs in order to fully evaluate environmental impact of Ag-NPs. The review focuses on the formation and transformation of Ag$_2$S-NPs from both thermodynamic and kinetic perspectives, particularly (i) the formation mechanism of Ag$_2$S in various environmental scenarios, (ii) redox transformation of Ag$_2$S caused by oxidation of S($-$II) and (iii) effects of environmental matrices on the formation and transformation processes. In most cases, sulfidation of Ag-NPs causes a dramatic decrease in their toxicity due to the extremely low solubility of Ag$_2$S, potentially restraining their short-term environmental impact. However, the transformation of Ag$_2$S-NPs with potential release of Ag$^+$ and *in situ* formation of Ag^0 and Ag^0/Ag$_2$S-NPs hetero-nanostructures may possibly increase the toxicity. Mechanistically-based kinetic modeling has been proposed here to quantitatively describe the rate and extent of the transformation of Ag$_2$S-NPs, with such models of value, at least, in validating proposed transformation mechanisms of Ag$_2$S-NPs and, at best, in predicting their transformation behaviors under realistic environmental conditions.

Environmental significance

Sulfidation of silver nanoparticles (Ag-NPs) readily occurs in both urban sewage systems and sulfur-rich natural environments with resultant formation of silver sulfide nanoparticles (Ag$_2$S-NPs). It is essential to understand the transformation and fate of Ag$_2$S-NPs to fully evaluate the environmental impact of Ag-NPs. The review focuses on the formation and transformation of Ag$_2$S-NPs from both thermodynamic and kinetic perspectives with particular attention given to (i) the formation mechanism of Ag$_2$S in various environmental scenarios and (ii) the redox transformation of Ag$_2$S caused by oxidation of S($-$II), resulting in improved understanding as to how the transformations of Ag$_2$S-NPs (with potential release of Ag$^+$ and *in situ* formation of Ag^0 and Ag^0/Ag$_2$S-NPs hetero-nanostructures) affect the toxicity of these nanoparticles in aqueous environments.

1. Introduction

Engineered nanomaterials (ENMs) are rapidly migrating from the laboratory bench into full-scale applications in many domains including optics, food, alternative energy, medical, environmental remediation, chemical engineering and consumer products.[2] Among these ENMs, silver nanoparticles (Ag-NPs) are one of the most common and are widely used in consumer and medical products because of their broad-spectrum bactericidal activity.[3] Due to the release of Ag-NPs into the aquatic environment during production, storage, transport and application,[4,5] concerns have recently been raised regarding the environmental safety and toxicity of these nanoparticles. Mass flow analysis indicates that most Ag-NPs released from domestic and industrial sources first enters the sewer system and then wastewater treatment

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† Electronic supplementary information (ESI) available: The supporting information includes two figures and nine equations to describe the thermodynamic calculation of oxysulfidation of Ag(0) and oxygenation of Ag$_2$S, thermodynamic calculation of Ag species in the presence of Cl$^-$ as well as the effect of dissolved oxygen on dissolution of Ag$_2$S-NPs. See DOI: 10.1039/c9en00138g

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plants (WWTPs).[6–8] Kaegi *et al.* showed that sulfidation of Ag-NPs occurs to various degrees due to the relatively high sulfide concentrations in sewer systems with these sulfidized Ag-NPs mostly associated with the suspended solids in the sewer system and, as such, efficiently transported to WWTPs without substantial loss to the sewer biofilms.[9,10] Ag_2S-NPs become and remain the dominant Ag species during waste-water treatment with the speciation of Ag exclusively detected as Ag_2S mostly in nano-sized (5–20 nm) particulate form in the digested sludge as well as in the effluent.[11,12] Whilst the type and source of Ag that enter WWTPs can vary and may include AgCl from textile discharge and/or silver thiosulfate

from photo processing discharge, these particles eventually form thermodynamically favorable Ag_2S.[10,13,14] Therefore, there are concerns regarding accumulation of Ag_2S-NPs in natural environments with adverse effects to organisms and human.

Because of the very low solubility of Ag_2S ($K_{sp} = \sim 10^{-51}$), Ag_2S-NPs have extremely low silver lability in aqueous environments.[14] A number of studies have shown that the sulfidation of Ag-NPs serves to reduce the acute toxicity of Ag species toward not only bacteria, such as *E. coli*, *S. oneidensis*, *B. subtilis* and nitrifying bacteria,[15–17] but also many higher organisms including *Danio rerio* (zebrafish), *Oncorhynchus*

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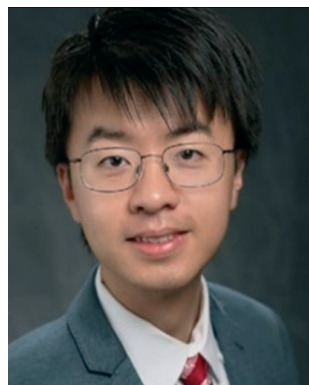
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mykiss (rainbow trout), *Fundulus heteroclitus* (killifish), *Caenorhabditis elegans* (nematode worm), *Lemna minuta* (least duckweed), *Chattonella marina* (algae), *Vigna unguiculata* L. Walp (cowpea), *Triticum aestivum* L. (wheat), *Cucumis sativus* (cucumber) and *Lactuca sativa* (lettuce).[18–25] However, recent studies showed that the oxidation of Ag_2S-NPs occurs in wastewater effluents as a result of the presence of various oxidants such as chlorine and ozone with subsequent release of Ag^+ and increasing toxicity to algae.[26,27] Recently, Li *et al.* reported that oxidation of Ag_2S-NPs occurred in irradiated natural waters in the presence of Fe(III) suggesting that the co-existence of Fe(III) and light is capable of driving solubilization of Ag_2S-NPs. As such, two main concerns exist regarding (i) the stability of Ag_2S-NPs against the oxidation of S(−II) with elution of Ag^+ and/or to form Ag^0 (ii) the toxicity of environmentally transformed Ag_2S-NPs to various organisms present in natural environments. This brief review begins with examination of the formation mechanism of Ag_2S-NPs *via* oxysulfidation, exchange and complexation reactions under various environmental conditions. Note that even though we discuss the pathways sulfidation of Ag-NPs, the reaction mechanism discussed here applies to other sources of Ag (such as AgCl and/or silver thiosulfate) as well. Since, sulfide is principally present as HS^- at circumneutral pH conditions representative of wastewaters and natural aqueous environment; we have used HS^- to refer to total sulfide from here on in our discussion. However, it is to be noted that both H_2S and HS^- play a role in Ag-NPs sulfidation as reported earlier.[28] The second section of the review discuss potential pathways for the oxidation of S(−II) resulting in the solubilization of Ag_2S-NPs with the release of Ag^+ in the presence of various oxidants. The photochemical properties of Ag_2S-NPs and redox transformations of Ag_2S-NPs under solar irradia-

tion in the presence of natural redox-active metal species (such as Fe(III)) are also discussed. The transformation kinetics of Ag_2S-NPs as well as the consequences of such transformation on the toxicity under conditions of environmental relevance are reviewed in detail with particular attention given to the possible formation of heterostructured Ag^0/Ag_2S-NPs assemblages. Finally, important issues requiring further investigation relating to the transformation of Ag_2S-NPs and their potential environmental effects are also presented.

2. Formation of Ag_2S-NPs: oxysulfidation, exchange and complexation reactions

2.1 Oxysulfidation reactions

Uncertainty exists regarding the mechanism of formation of Ag_2S-NPs *via* the interaction of Ag-NPs with HS^- under environmentally relevant conditions. Recently, Liu *et al.* investigated the sulfidation of Ag-NPs to $Ag_2S(s)$ in the presence of HS^- and dissolved oxygen (DO) and suggested that the sulfidation pathway varies depending on competing rates of oxidative dissolution and direct oxysulfidation.[28] At high sulfide concentrations, Ag-NPs oxysulfidation and resultant formation of $Ag_2S(s)$ occurs by a direct particle-fluid reaction with Ag^+ sequestered by sulfide before dissolved species appear, while at low sulfide concentrations, the sulfidation pathway switches from direct oxysulfidation to an oxidative dissolution/precipitation mechanism in which soluble Ag^+ is generated as an intermediate.[28] However, the mechanism of oxidative dissolution still remains controversial. One view is that the release of Ag^+ due to the removal of a Ag silver oxide coating while the other idea shows that the release of Ag^+ is

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the result of the formation of subvalent Ag (*i.e.* $\equiv Ag_3OH^0$) with the subsequent formation of protective oxidized Ag layers (*i.e.* Ag_6O octahedral) preventing the further oxidation of AgNPs.[29,30] Kent *et al.* employed arrays of immobilized Ag-NPs fabricated by nanosphere lithography to investigate the Ag-NP sulfidation mechanism.[12] The observation of an increase in height of the immobilized Ag-NPs upon sulfidation together with formation of a non-uniform passivating layer of Ag_2S around a core of AgNPs provided clear evidence that sulfidation occurs *via* a heterogeneous mechanism at high S/Ag molar ratio (40:1 to 400:1).[12] Levard *et al.* observed the formation of acanthite (Ag_2S) nanobridges between Ag-NPs at low S/Ag molar ratio implying that Ag_2S formation occurs *via* a dissolution/precipitation mechanism.[31] In their following study, three distinct morphologies of Ag-NPs following sulfidation were observed including a core/shell structure, acanthite bridges between Ag-NPs and precipitates of isolated acanthite, further suggesting that the S/Ag molar ratio plays an important role in formation of particular Ag_2S structures.[16] Thermodynamically, however, the co-existence of oxygen and sulfide should not happen in aqueous environment. As such, the oxygen-mediated oxysulfidation pathway will only occur as a result of the sequential presence of these reactants but with kinetic limitations to mixing and/or diffusion preventing their co-existence. It is also possible for anthropogenic Ag-NPs to experience partial (surface) oxidation before reaching the anaerobic wastewater environments with this process potentially providing the Ag(I) which reacts with sulfide to form Ag_2S. Trace levels of O_2 arising from continuous wastewater influent may well maintain the driving force for eqn (1).

$$4Ag(0) + O_2 + 2HS^- + 2H^+ \rightarrow 2Ag_2S + 2H_2O \qquad (1)$$
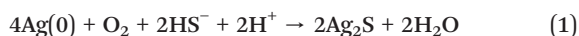
Assuming a strict oxygen-free system in highly reducing environments, another alternative pathway for Ag(0) sulfidation is possibly *via* reduction of protons yielding H_2. Conventionally Ag(0) is regarded as an inert noble metal with respect to reaction with protons, however the extremely low solubility of Ag_2S could thermodynamically enable the evolution of H_2. Such a mechanism is analogous to the proposed mechanisms for FeS transformation to FeS_2 in which oxidation of FeS (sulfur specifically) proceeds through the reduction of protons (eqn (2)).[32]

$$FeS + HS^- + H^+ \rightarrow FeS_2 + H_2 \qquad (2)$$
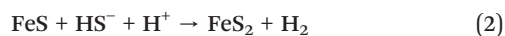
The formation of Ag_2S *via* reaction of Ag(0) with HS^- (eqn (3)) may serve as an alternative mechanism to bypass the requirement of an external oxidant thereby enabling the transformation to proceed in a completely anoxic environment.

$$2Ag(0) + HS^- + H^+ \rightarrow Ag_2S + H_2 \qquad (3)$$

Based on thermodynamic calculation, the value of ΔG for the reaction shown in eqn (3) remains negative as long as the

concentration of HS^- exceeds 4 nM with this result implying that Ag-NPs could, in theory, be sulfidized without the involvement of O_2 under strict anoxic conditions (ESI† Fig. S1). It should be noted that there is no experimental evidence to support that such a reaction could occur on a realistic timeframes.

Note that while we have discussed the role of HS^- in Ag-NPs sulfidation in detail here, polysulfides, which may also exist in wastewater treatment plant, are also expected to result in sulfidation of AgNPs possibly resulting in formation of dissolved Ag(I) polysulfide complexes as reported earlier.[33]

2.1.1 Effect of pH, ionic strength and particle size. Sulfidation of Ag-NPs also depends on the solution conditions (such as pH, ionic strength) as well as Ag-NP particle size. With the shift in pH from alkaline to neutral/acidic conditions, the oxysulfidation rate of Ag-NPs increases with this increase most likely attributed to (i) the more rapid oxidative dissolution of Ag-NPs at lower pHs and/or (ii) stronger electrostatic repulsion between negatively charged Ag-NPs and HS^- (the dominant sulfide species) at higher pHs.[28,34] The sulfidation of Ag-NPs was observed to be enhanced with increase in the ionic strength.[35] While a less negative zeta potential may lead to aggregation of Ag-NPs at higher ionic strength, the change in zeta potential also contributes to a significant decrease in the electrostatic repulsion between HS^- and Ag-NP surfaces, consequently promoting sulfidation.[35] The presence of divalent Ca^{2+} and Mg^{2+} also enhances the sulfidation rate of Ag-NPs by nearly 2–3 fold compared to that observed in the presence of Na^+ and K^+ with this effect possibly due to the stronger charge screening by higher valence cations and the resultant increased extent of interaction between sulfide and Ag-NPs.[35] Since the radius of Ca^{2+} (0.114 nm) is larger than that of Mg^{2+} (0.086 nm), the compression of the electric double layers and cation-bridging effect by Ca^{2+} is stronger than is the case for Mg^{2+}, leading to faster sulfidation of Ag-NPs in the presence of Ca^{2+} compared to that observed in the presence of Mg^{2+} at the same ionic strength.[35] Since there was no obvious increase in the release of Ag^+ in the presence of Na^+, K^+, Ca^{2+} and Mg^{2+}, it would seem reasonable to conclude that the enhancement in the corresponding sulfidation rates of Ag-NPs in the presence of these ions occur through direct oxysulfidation mechanism.[28] Increasing the Ag-NP primary size reduces the reaction rate for this heterogeneous process as a result of decrease in the specific surface area.[9,28,35,36] According to the kinetic law reported for the sulfidation of Ag-NPs by Liu *et al.*,[28] the heterogeneous reaction between Ag-NPs and sulfide can be considered as homogeneous reactions on the basis of a mole of silver atoms and the effect of change of particle size in Ag-NPs on their reactivity is simply reflected through the following kinetic law (eqn (4)),[35]

$$-d[\text{sulfide}]/dt = (k_{Ag} \times [\text{Ag-NPs}]_0 + k') \times [\text{sulfide}] \qquad (4)$$

where k_{Ag} and k' are the rate constants for sulfidation of Ag-NPs and depletion of sulfide, respectively. According to

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Zhang *et al.*,[35] the sulfidation rate constant for 10 nm Ag-NPs is 1.9 mM^{-1} h^{-1}, which is nearly 2-fold higher than that observed for 40 nm Ag-NPs.[16,35] Zhang *et al.* also found that there is a positive linear relationship between the sulfidation rate constant and the surface area (S_{Ag}) of Ag-NPs, where surface area-normalized sulfidation rate constant (k_s) can be estimated to be 0.032 g m^{-2} mM^{-1} h^{-1} ($R = 0.98$, $p < 0.02$) using a range of Ag-NPs with varying primary sizes (eqn (5)).[35]

$$-d[\text{sulfide}]/dt = (k_S \times S_{Ag} \times [\text{Ag-NPs}]_0 + k') \times [\text{sulfide}] \qquad (5)$$

Not only the primary particle size but also aggregation state of Ag-NPs affects the sulfidation processes. It has been shown that the rate of sulfidation of Ag-NPs decreases with the increase in diameter of primary particles (by a factor of 1.1–1.4) and with broader size/height distribution.[12,16,37,38] Because of the larger average particle size and polydispersity, sulfidation of the larger particles with diameters of 30–80 nm and aggregates (of up to several hundred nanometers in size) is kinetically limited compared with that of smaller Ag-NPs (with a size of 30 nm or less) and was not complete even after 48 h.[16] Similarly, with aggregation of sulfidized Ag-NPs, where Ag$_2$S forms nano-bridges between the Ag-NPs, the sulfidation rate decreased with time during Ag-NP exposure to Na$_2$S.[31]

2.1.2 Impact of natural organic matter. Natural organic matter (NOM) is ubiquitous in natural aqueous environments and influences the rate and extent of Ag-NP dissolution and aggregation.[34,39–41] The impact of NOM on the sulfidation process, however, is controversial. On one hand, the presence of humic acid (HA) was observed to increase the sulfidation rate of particulate Ag-NPs, which was explained based on improvement in the colloidal stability of Ag-NPs in the presence of NOM.[28,36,42] Under some circumstances, however, aggregation as a result of inter-particle bridging through the complexation between Ca^{2+} and carboxylic groups within HA could outcompete steric hindrance exerted by HA, resulting in the destabilization of Ag-NPs[43] and hence in such cases the presence of NOM may not increase the Ag-NPs sulfidation rate. The sulfidation of immobilized Ag-NPs coated onto solid substrates by nanosphere lithography appears to be little affected by the presence of HA,[12] further implying that HA-mediated stabilization/destabilization of Ag-NPs and some other factors plays an important role in the sulfidation of Ag-NPs. Apart from the change of stability of Ag-NPs, the presence of NOM also affects the migration of HS$^-$ to the Ag-NP surface, thereby influencing the sulfidation process. Zhang *et al.* showed that the rate of sulfidation of Ag-NPs decreases in the presence of NOM, possibly due to an increase in the electrostatic repulsion between the negatively charged Ag-NPs (due to sorption of NOM) and HS$^-$.[35] On the contrary, the adsorption of HS$^-$ on the HA surface may facilitate the sulfidation of Ag-NPs by improving the transport of HS$^-$ to the Ag-NP surface.[36] In addition, the presence of NOM may

also impact the oxidative dissolution of AgNPs by blocking the reactive sites on AgNPs surface which, in turn, may impact the formation of Ag$_2$S *via* oxidative dissolution/precipitation mechanism.[28] Overall, based on the current literature, it appears that the impact of NOM on Ag-NPs sulfidation is governed by two main factors; namely (i) Ag-NPs stabilization (towards aggregation) and reactivity (towards dissolution) and (ii) HS$^-$ adsorption on the Ag-NPs surface. While the impact of NOM on Ag-NPs stability and reactivity is governed by a range of factors including NOM type and concentration with NOM containing high molecular weight moieties expected to stabilize AgNPs to a larger extent than low molecular weight NOM fractions.[44,45] Furthermore, since sulfur containing groups such as thiols strongly bind metallic silver while reduced sulfur and nitrogen groups bind Ag(I),[46] it is expected that NOM higher in sulfur and nitrogen content will bind AgNPs more strongly and result in a decrease in the dissolution rate of Ag-NPs to a larger extent than that observed in the presence of NOM low in sulfur and nitrogen content as reported earlier.[46] The low-molecular weight hydrophilic organic moieties in NOM such as carboxylic and phenolic groups do not interact strongly with AgNPs and/or Ag(I) and hence the presence of these organic moieties is unlikely to have any major impact on Ag-NP stability and reactivity.[46] The impact of NOM on adsorption of HS$^-$ to the Ag-NP surface is expected to be dependent on the NOM type and concentration as well as other solution conditions such as pH. In the presence of high molecular weight organic moieties, the adsorption of HS$^-$ on Ag-NPs surface is likely to be inhibited to a larger extent compared to that observed in the presence of low-molecular weight organic moieties due to larger steric hindrance. The solution pH will also impact the speciation (and consequently charge) of NOM and sulfide as well as the charge on the Ag-NPs surface with these pH dependent phenomena impacting the adsorption of sulfide on the Ag-NPs surface. For example, pH < 7 is expected to be more favorable for adsorption since neutral H$_2$S is the dominant sulfur species under these conditions and its adsorption will not be electrostatically hindered. Overall, due to a range of factors affecting on Ag-NPs sulfidation in the presence of NOM, the impact of NOM cannot be generalized and needs to be examined on a case by case basis.

2.2 Exchange and complexation reactions

Ag$_2$S can also be formed by Ag(I) exchange reactions in different metal sulfides. The hypothesis of metal replacement is that more strongly S(−II)-bound metals will substitute more weakly bound metals and the exchange of divalent metals (Me) with Ag(I) can be represented by eqn (6):[47]

$$2Ag(\text{I}) + MeS \rightleftharpoons Me(\text{II}) + Ag_2S \qquad (6)$$
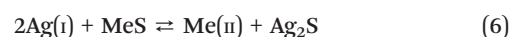
Previous studies have reported that the metal sulfides with higher solubility sulfides, *i.e.* Fe(II), Cd(II), Pb(II), Zn(II) and

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As(III) sulfides, are subject to exchange with Ag(I), Hg(II) and Cu(II) which form precipitated sulfides with lower solubility.[47,48] Similarly, formation of discrete Ag_2S particles following the sorption of Ag(I) on pyrite and amorphous FeS was observed[49,50] with this observation further supporting the hypothesis that Ag(I) replaces other metals that are relatively weakly bounded to S(−II). In addition, Ag-NPs were also observed to transform into Ag_2S on reaction with other metal sulfides (such as CuS and ZnS) under oxic conditions (where free sulfide is absent).[51] The sulfidation of Ag-NPs obeyed pseudo first-order kinetics in the presence of metal sulfides (eqn (7)),[51]

$$[Ag\text{-NPs}]_t = [Ag\text{-NPs}]_0 \times e^{-kt} \qquad (7)$$

with the rate constant (k) increasing with increase in metal sulfide concentration and decrease in the size of Ag-NPs, which was described by the following equation (eqn (8)):[51]

$$k = k' \times [MS]_{\text{initial}}^{a} \times (1/d_{Ag\text{-NPs}})^{b} \qquad (8)$$

where the exponents a and b as well as k' were derived by fitting the experimental data via nonlinear least-squares regression.[51] It should be noted that the rate of reaction between Ag-NPs and metal sulfides also depends on the species (e.g. ZnS and CuS) and crystallinity of the metal sulfides.[51] In addition to ion exchange reactions, the interaction between Ag-NPs and organic sulfur (e.g. thiols, cysteine, glutathione) have been shown to result in the formation of various types of Ag–S compounds with different structures.[47] Core–shell structures were observed on reaction of Ag-NPs with organic sulfur to form Ag-organic sulfur and Ag_2S-like complexes on the Ag-NP surface.[52,53] For example, the adsorption of organothiols (e.g. p-methylbenzenethiol, p-benzenedithiol and 2-mercaptobenzimidazole) onto Ag-NPs occurred predominately through reaction with Ag_2O present on the Ag-NP surfaces with subsequent formation of Ag–SR complexes on the surface, while the interaction of organic thiol allylmercaptan with Ag-NPs results in the formation of core–shell structures with metallic Ag cores surrounded by Ag_2S-like phase.[55] It is also noted that the complexation of Ag(I) with thiols affects the cation exchange reaction, resulting in a reduced amount of Ag(I) adsorbed onto Fe sulfides.[49,50]

3. Transformation of Ag_2S-NPs: non-redox and redox reactions

3.1 Non-redox reactions

Although Ag_2S-NPs are subject to be formed via exchange reactions (eqn (5)), it has been reported that Ag_2S-NPs can release small amounts of Ag^+ through cation exchange reactions between Ag(I) within Ag_2S and Fe(III) in the dark with the subsequent formation of FeS.[1] In the human body, although the much lower abundance of selenide relative to sulfur makes it unlikely to compete with sulfur kinetically
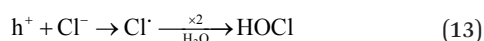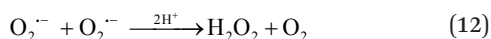
during its reaction with silver surfaces, the incorporation of Se in argyrial deposits was observed, which could be attributed to the even higher insolubility for Ag_2Se (K_{sp} = 3.1 × 10^{-65}) making the exchange reaction thermodynamically favorable.[54] Anion exchange reactions with Cl^- and thiosulfate (which is often present in fertilizer) have also been observed to facilitate the dissolution of $Ag_2S(s)$, resulting in a significant increase in the bioavailability of Ag to plants via root uptake.[20,55,56] The formation of dissolved AgCl complexes can drive dissolution of Ag_2S, though the Cl^--mediated dissolution of Ag_2S is expected occur only at elevated Cl^- concentrations (>200.0 mM) (ESI† Fig. S2). Given the high affinity of Ag(I) for thiols,[57] the formation of Ag(I)-thiol complexes may induce the dissolution of Ag_2S-NPs with recent results showing that up to 25% of Ag was bound to thiols when the roots were treated with Ag_2S-NPs.[58] Interestingly, NOM was observed to either enhance or inhibit dissolution of Ag_2S by either ligand-promoted processes or steric protection, respectively.[59,60] One important factor influencing the role of NOM in dissolution of Ag_2S is the content of reduced S moieties (i.e. thiols). For example, Pony Lake fulvic acid (PLFA) has a higher total sulfur content (2.6%) than Pahokee peat fulvic acid (PPFA) (0.63%) or Suwannee River fulvic acid (SRFA) (0.48%) with this result consistent with the observation that PLFA increased while SRFA and PPFA decreased the release of dissolved Ag from Ag_2S-NPs.[61]

3.2 Redox reactions

Because of the extremely low solubility of $Ag_2S(s)$, the mobilization of Ag_2S through complexation by thiols and/or exchange reactions with other metal is difficult, however oxidation of S(−II) in the presence of various strong oxidants such as chlorine and ozone (O_3) may result in the solubilization of Ag_2S-NPs.[26,27] Thalmann et al. showed that O_3 can mobilize Ag_2S-NPs in wastewater effluents as a result of oxidation of HS^- to SO_4^{2-}.[26] Recently, Li et al. reported that Ag_2S-NPs also undergoes dissolution in surface waters containing free chlorine forming dissolved Ag(I), suggesting that not only hypochlorite but also chlorine radicals and/or hydroxyl radicals are involved in the oxidation of Ag_2S-NPs.[27] However, the mechanism for formation of chlorine radicals and/or hydroxyl radicals in this system still remain unclear. Unlike the above strong oxidants (i.e. chlorine and ozone), there is no evidence that oxygen can solubilize $Ag_2S(s)$ although the oxygenation of $Ag_2S(s)$ is thermodynamically favored (ESI† eqn (S7)–(S9)). This observation thus suggests that the oxidation of $Ag_2S(s)$ by oxygen is extremely slow.

Since Ag_2S-NPs can serve as a direct low bandgap semiconductor material (E_g = ~1.0 eV),[62] irradiation with solar light may further facilitate the oxidative dissolution of Ag_2S-NPs as a result of generation of various oxidants such as reactive oxygen species (ROS such as $HO^{\bullet}$ and H_2O_2) and/or organic radicals. Garg et al. recently reported that under

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visible light irradiation of AgCl(s) (eqn (9)), the photo-generated electrons in the conduction band reduce Ag(I) to Ag^0 (eqn (10)) with the elemental silver particles so formed coalescing and aggregating to form Ag-NPs and/or reduce O_2 to form $O_2^{•-}$ (eqn (11)) which disproportionates to form H_2O_2 (eqn (12)). The photogenerated holes in the valence band result in the generation of free chlorine *via* the oxidation of Cl^- (eqn (13)).[63]

$$AgCl \xrightleftharpoons{h\nu} e^- + h^+ \qquad (9)$$

$$e^- + Ag(I) \rightarrow Ag^0 \qquad (10)$$

$$e^- + O_2 \rightarrow O_2^{•-} \qquad (11)$$

$$O_2^{•-} + O_2^{•-} \xrightarrow{2H^+} H_2O_2 + O_2 \qquad (12)$$

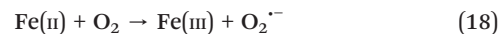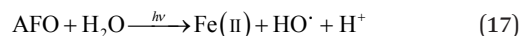$$h^+ + Cl^- \rightarrow Cl^• \xrightarrow[H_2O]{\times 2} HOCl \qquad (13)$$

A similar mechanism can be hypothesized to occur in the presence of Ag₂S-NPs with photo-generated holes inducing the formation of $HO^•$ and SO_4^{2-} (eqn (14) and (15)) and electrons in the conduction band resulting in formation of ROS and/or AgNPs (eqn (10) and (11)).

$$h^+ + H_2O \rightarrow {}^•OH + H^+ \qquad (14)$$

$$h^+ + S^{2-} \xrightarrow{2O_2} SO_4^{2-} \qquad (15)$$
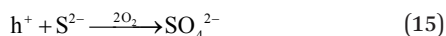
Although there is no evidence confirming that the photo-transformation of Ag₂S-NPs to Ag-NPs and SO_4^{2-} occurs in natural waters, transformation of Ag₂S to Ag-NPs was observed on incineration of the sewage sludge containing Ag₂S-NPs.[64,65] Furthermore, the presence of Ag₂S-NPs has been shown to have the potential to accelerate the photo-degradation of NOM.[1,66,67] However, whether the degradation of NOM originates from oxidation by photogenerated holes (and its subsequent oxidation products), *via* interaction between Ag₂S and NOM with enhancement of photo-transformation of NOM and/or simply as a result of adsorption of NOM on the Ag₂S surface remains unclear. Li *et al.* further showed that dissolution of Ag₂S-NPs occurs on irradiation with simulated sunlight in the presence of Fe(III).[1,66] Whilst both electron spin resonance and *tert*-butyl alcohol scavenging results confirmed the formation of $HO^•$ in the system,[1] the mechanism of the formation of $HO^•$ is not clear. The ligand-to-metal charge transfer (LMCT) pathway could be invoked to explain the generation of ROS in irradiated Ag₂S suspension containing Fe(III) namely, LMCT within Fe(III) species (*e.g.* amorphous ferric oxide, AFO or dissolved inorganic Fe(III) species) results in the formation of Fe(II) and $HO^•$ (eqn (16) and (17)). The Fe(II) so-formed further undergoes oxygenation reaction resulting in H_2O_2 generation (eqn (12), (18)

and (19)) and subsequently H_2O_2-mediated formation of $HO^•$ *via* the Fenton reaction (eqn (19)).

$$Fe(III) + Fe(III) \rightarrow AFO \qquad (16)$$

$$AFO + H_2O \xrightarrow{h\nu} Fe(II) + HO^• + H^+ \qquad (17)$$

$$Fe(II) + O_2 \rightarrow Fe(III) + O_2^{•-} \qquad (18)$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^• + OH^- \qquad (19)$$

The photo-generated $HO^•$ can subsequently oxidize Ag₂S to form Ag(I) and SO_4^{2-} (eqn (20) and (21))

$$Ag_2S + HO^• \rightarrow Ag(I) + \text{Intermediate} \qquad (20)$$

$$\text{Intermediate} + HO^• \rightarrow Ag(I) + SO_4^{2-} \qquad (21)$$

With the Fe(III)-dependent photo-induced dissolution of Ag₂S-NPs, the formation of Ag^0 was observed,[1] suggesting that the reduction of Ag(I) to Ag^0 takes place. Under aerobic conditions, the oxygenation of Fe(II) can generate $O_2^{•-}$ (eqn (18)) which can reduce Ag(I) to Ag^0 (eqn (22)).[61]

$$Ag(I) + O_2^{•-} \rightarrow Ag^0 + O_2 \qquad (22)$$
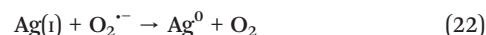
This mechanism of $O_2^{•-}$-mediated reduction of Ag(I) to Ag^0 complies with the observation in Li *et al.*'s work that the presence of O_2, as the source of $O_2^{•-}$, inhibited the oxidative dissolution of Ag₂S-NPs.[66]

To validate the above hypothesized reaction mechanism, a numerical kinetic model of reaction schemes has been proposed by use of KinTek or Kintecus software.[68–70] Modelling results based on the reaction scheme discussed above was developed here (Table 1), with the core components of this mechanism including (i) LMCT pathway within Fe(III) species with resultant formation of $HO^•$, (ii) $HO^•$-mediated oxidation of S(−II) with the release of Ag^+ and (iii) the reduction of Ag^+ to Ag^0 *via* the electron charging–discharging model. The model results depicting the release of Ag^+ and SO_4^{2-} from oxidation of Ag₂S-NPs and the reduction of Fe(III) to Fe(II) as well as the effect of dissolved oxygen on the dissolution of Ag₂S-NPs are illustrated in Fig. 1 and ESI† Fig. S3, respectively, with the excellent model fittings for the experimental data providing confidence in the value of this modelling approach to elucidate the reaction mechanisms. In our previous work, such kinetic modelling approaches have been extensively used, particularly with regard to identifying possible reaction mechanism in ROS-related processes such as Fenton and Fenton-like reactions in both natural and engineering system, and found to be very robust.[71–78] At worst, such an approach is invaluable for mechanism hypothesis testing and, at best, will enable to construct mechanistically-based kinetic models with capacity to predict the transformation behavior of Ag₂S-NPs under conditions of environmental relevance.

In natural aqueous environments, the role of NOM must be carefully considered. NOM may not only complex Fe (both Fe(II)

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Table 1 Kinetic model (reaction mechanism II) to predict dissolution of Ag_2S under light irradiation of Ag_2S-NPs[a]

No.	Reaction	Rate constant	Ref.
Fe-Mediated ROS generation			
1	$Fe(III) + Fe(III) \rightarrow AFO^b$	$3.0 \times 10^5 \ M^{-1} \ s^{-1}$	71
2	$AFO \rightarrow Fe(III) + nH^+$	$4.8 \times 10^{-6} \ s^{-1}$	72
3	$AFO \xrightarrow{hv} Fe(II) + HO^{\cdot}$	$1.5 \times 10^{-4} \ s^{-1}$	73
4	$Fe(III) \xrightarrow{hv} Fe(II) + HO^{\cdot}$	$5 \times 10^{-4} \ s^{-1}$	73
5	$Fe(II) + O_2 \rightarrow Fe(III) + O_2^{\cdot-}$	$0.5 \ M^{-1} \ s^{-1}$	74
6	$Fe(III) + O_2^{\cdot-} \rightarrow Fe(II) + O_2$	$1.5 \times 10^8 \ M^{-1} \ s^{-1}$	75
7	$Fe(II) + O_2^{\cdot-} \xrightarrow{2H^+} Fe(III) + H_2O_2$	$2.4 \times 10^6 \ M^{-1} \ s^{-1}$	75
8	$Fe(II) + H_2O_2 \xrightarrow{2H^+} Fe(III) + HO^{\cdot} + H_2O$	$55.0 \ M^{-1} \ s^{-1}$	75
9	$Fe(II) + HO^{\cdot} \xrightarrow{2H^+} Fe(III) + H_2O$	$3.2 \times 10^8 \ M^{-1} \ s^{-1}$	75
10	$O_2^{\cdot-} + O_2^{\cdot-} \xrightarrow{2H^+} H_2O_2 + O_2$	$5.0 \times 10^7 \ M^{-1} \ s^{-1}$	77
11	$HO^{\cdot} + O_2^{\cdot-} \xrightarrow{H^+} H_2O + O_2$	$7.5 \times 10^9 \ M^{-1} \ s^{-1}$	75
12	$HO^{\cdot} + HO^{\cdot} \rightarrow H_2O_2$	$5.2 \times 10^9 \ M^{-1} \ s^{-1}$	75
S(−II) oxidation reactions			
13	$Ag_2S + HO^{\cdot} \xrightarrow{hv} Ag(I) + Intermediate$	$4.0 \times 10^4 \ M^{-1} \ s^{-1}$	This study
14	$Intermediate + HO^{\cdot} \xrightarrow{hv} Ag(I) + SO_4^{2-}$	$4.0 \times 10^5 \ M^{-1} \ s^{-1}$	This study
15	$Ag(I) + O_2^{\cdot-} \xrightarrow{AgNPs} Ag^0 + O_2$	$2.0 \times 10^5 \ M^{-1} \ s^{-1}$	76, 77

[a] pH = 5.0. [b] AFO represents amorphous ferric oxide.

and $Fe(III)$) (eqn (23)) affecting the redox potential of the $Fe(III)/Fe(II)$ redox couple but may also mediate the direct reduction of

Fig. 1 Light irradiation induced dissolution (Ag^+ release and SO_4^{2-}) kinetics of Ag_2S-NPs in the presence of $Fe(III)$. Symbols are experimental data from Li et al.;[1] lines in Fig. 1 are the model fittings based on reaction scheme I (Table 1). Experimental conditions: [Ag_2S-NPs]$_0$ = 5.0 mg L^{-1}; [$Fe(III)$]$_0$ = 2.0 mg L^{-1}; pH = 5.0. [DO] = 8 mg L^{-1}. Reprinted with permission from the American Chemical Society.

$Ag(I)$ released on Ag_2S dissolution to Ag^0 (eqn (24)).[79] Interestingly, the formation of an $Fe(III)$ complex with NOM will result in a decrease in the redox potential of the $Fe(III)/Fe(II)$ couple (eqn (25)), providing additional driving force for the reduction of $Ag(I)$ thereby enhancing the formation of Ag^0-NPs.[80]
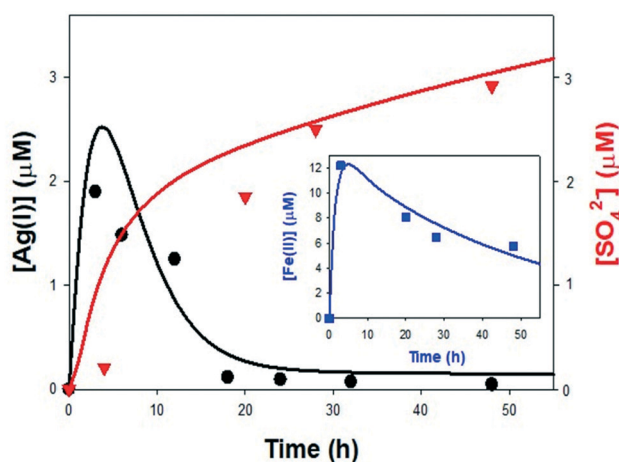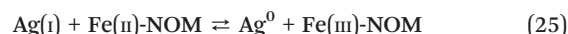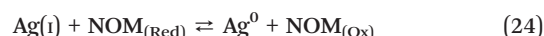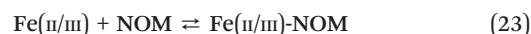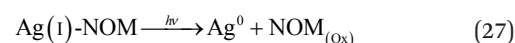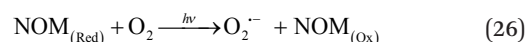
$$Fe(II/III) + NOM \rightleftharpoons Fe(II/III)\text{-}NOM \quad (23)$$

$$Ag(I) + NOM_{(Red)} \rightleftharpoons Ag^0 + NOM_{(Ox)} \quad (24)$$

$$Ag(I) + Fe(II)\text{-}NOM \rightleftharpoons Ag^0 + Fe(III)\text{-}NOM \quad (25)$$

On irradiation, the NOM-mediated formation of Ag^0-NPs may be further enhanced[79] as a result of formation of $O_2^{\cdot-}$ (eqn (26)), which further contributes to the reduction of $Ag(I)$ to Ag^0 (eqn (22)) and/or LMCT in $Ag(I)$-NOM complex (eqn (27)).

$$NOM_{(Red)} + O_2 \xrightarrow{hv} O_2^{\cdot-} + NOM_{(Ox)} \quad (26)$$

$$Ag(I)\text{-}NOM \xrightarrow{hv} Ag^0 + NOM_{(Ox)} \quad (27)$$

The $O_2^{\cdot-}$-mediated reduction of $Ag(I)$ to Ag^0 process can be catalyzed by the presence of Ag-NPs via the electron

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charging–discharging mechanism with the formation of new clusters of Ag-NPs with much smaller size (eqn (28)–(30)).[76,77,81] These smaller Ag-NPs particles might be expected to exhibit much higher reactivity[76] and be more mobile than the original Ag_2S-NPs,[82] thereby posing potential risks to aqueous environments.

$$Ag\text{-}NPs + O_2^{\bullet-} \rightarrow Ag\text{-}NPs*^- + O_2 \qquad (28)$$

$$Ag\text{-}NPs*^- + O_2 \rightarrow Ag\text{-}NPs + O_2^{\bullet-} \qquad (29)$$

$$Ag\text{-}NPs*^- + Ag(I) \rightarrow Ag\text{-}NPs + Ag^0 \qquad (30)$$

pH is an important parameter in controlling the redox transformation of various elements in natural waters, which not only affects the direct transformation of Ag_2S-NPs but also controls Ag_2S transformation through Fe redox chemistry. Firstly, pH can strongly affect the disproportionation of $O_2^{\bullet-}$ (eqn (12))[83] with subsequent variation in the formation of Ag^0-NPs via $O_2^{\bullet-}$-mediated reduction of Ag(I) to Ag^0-NPs (eqn (28)–(30))[77] affecting the oxidative dissolution of Ag_2S-NPs. Secondly, the rate of Fe(II) oxygenation (eqn (18)) decreases with decrease in pH, thereby inhibiting H_2O_2 production and consequently $HO^{\bullet}$ formation via Fenton-like reactions. However, at low pH, Fe(III) is much more soluble making Fe(III) much more photo-reactive with resultant increase in the rate of generation of $HO^{\bullet}$. Thirdly, Garg et al. showed that semiconducting AgCl(s) is much more photo-reactive under alkaline conditions compared to acidic conditions (eqn (9))[63] with similar behavior possibly expected for semiconducting Ag_2S.

In sulfur-rich environments, the coordination of eluted Ag(I) with HS^-/thiols and/or sulfidation of in situ formed Ag^0-NPs will finally result in the reformation of Ag_2S-NPs, initiating redox cycling of Ag_2S–Ag(I)–Ag^0–Ag_2S as shown in Fig. 2. It should also be noted that hetero-nanostructured assemblages of Ag^0/Ag_2S may likely be formed during the redox transformation of Ag_2S-NPs. Since the heterojunction or interface of metal-semiconductors within these heterostructures could enhance the separation efficiency of the photogenerated electrons (e^-) and holes (h^+), these Ag^0/Ag_2S heterostuctures m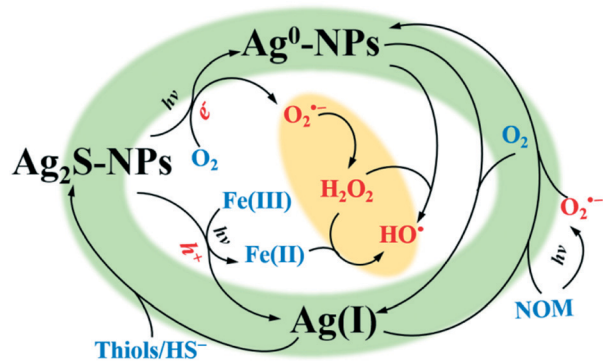ay display unique photocatalytic and antibacterial properties,[62,84,85] which might have unexpected adverse impacts in natural environments. Taken together, fundamental understanding on the effects of light on the interplay among Ag species, environmental matrices (e.g. NOM and Fe species) and ROS as well as the structural interconversion among Ag_2S-NPs, Ag(I) and Ag^0-NPs requires comprehensive evaluation.

4. Effects of Ag2S-NPs transformation on toxic effects

One well-accepted effect of sulfidation of Ag-NPs is that it can severely alleviate the toxicity by limiting the elution of soluble Ag^+ because of the extremely low solubility of Ag_2S.[18–25] Although Ag_2S-NPs may still display some nanotoxic effects, the inhibitory effect of Ag_2S-NPs is the lowest among Ag^+, Ag-NPs and Ag_2S-NPs with the same dosage of Ag.[15–17,86] Until recently, the rapid release of Ag^+ from Ag_2S-NPs under light irradiation in the presence of Fe(III) and/or when treated by oxidants such as free chlorine and ozone implies that Ag_2S-NP stability and safety may be overestimated necessitating further consideration of impacts of transformation of Ag_2S-NPs on toxicity.[1,66] Key issues that must be addressed in this regard are presented below.

First of all, photo-induced dissolution of Ag_2S-NPs with the release of Ag^+ must be taken into account in assessing toxicity not only attacks the enzymes of the respiratory chain reaction (e.g. NADH dehydrogenase) leading to the disengagement of respiration from ATP synthesis[87] but also binds with membrane transport proteins causing proton leakage with the breakdown of proton motive force.[88,89] The complexation between Ag^+ and glutathione (GSH) reductase or other GSH maintenance enzymes reduces the GSH/glutathione disulfide (GSSG) ratio with subsequent increase in excess ROS accumulation in the cell[90] leading to a collapse of membrane and mitochondrial function or damage to DNA replication.[91] These interactions with respiratory and transport proteins are most likely attributed to the high affinity of Ag^+ for thiol groups present in the cysteine residues of those proteins.[88,92] When considering significant concentrations (in the order of μM) of inorganic sulfur (e.g. HS^-) and organosulfur compounds (e.g. cysteine, glutathione, mercaptopropionate) in natural aqueous environments,[47] free Ag^+ ions may be present at extremely low concentrations or may even be non-existent. These sulfur ligands can effectively bind Ag^+ to form Ag(I) thiolates and/or Ag_2S, preventing the complexation between Ag^+ and thiol groups within the respiratory and transport proteins and thus potentially protecting against the acute toxic effects of Ag^+.[19,93,94] In brackish waters or seawaters, AgCl(s) precipitates and/or negatively charged $AgCl_n^{1-n}$ form and accumulate very slowly in organisms with resultant detoxification effects.[18,19,95]

Secondly, the oxygenation of Fe(II) or photo-irradiation of NOM produces $O_2^{\bullet-}$, which can mediate the reduction of Ag(I) released on Ag_2S dissolution to form Ag-NPs. These in situ formed Ag-NPs show far smaller size and higher reactivity

Fig. 2 Schematic presentation of the photochemical transformation of Ag_2S-NPs in natural aqueous environments.

than primary Ag$_2$S-NPs.[1] As such, the light-induced transformation of Ag$_2$S-NPs may not only exert toxic effects as a result of the presence of Ag$^+$ but also induce NP-specific toxic effects. Specifically, Ag-NPs have been reported to exert particle-specific effects resulting in pitting of cell membranes and eventual cell death as a consequence of the increase in membrane permeability and damage to cell membrane integrity.[93,96] Microscopy results have shown that the cells can internalize Ag-NPs following association with cell membranes, where cellular uptake of Ag-NPs may involve a passive diffusion for the small sized nanoparticles and/or phagocytosis of large-scale agglomerates.[90] The direct contact between Ag-NPs and cell membrane may inevitably cause the dissolution of particles followed by internalization of Ag$^+$ with this route of cellular uptake and toxicity mode usually considered to be particle-specific.[93,94] The internalized Ag-NPs together with solubilized Ag(I) within the cell can (i) interfere with sulfur-containing enzymes on the respiratory chain and membrane transport proteins with dissipation of the proton motive force for ATP synthesis and (ii) inhibit antioxidant defences with accumulation of intracellular ROS inducing the collapse of DNA replication.[87,90] The laboratory tests of NP-mediated release of Ag$^+$ might overestimate acute silver toxicity however Ag$^+$ binding by natural ligands (e.g. NOM, thiols/HS$^-$, Cl$^-$), present in abundance in the natural aqueous environment, will markedly reduce Ag$^+$ toxicity. On the contrary, the AgNP-specific toxic effects may lead to pronounced toxicity through the internalization of Ag$^+$ following cellular contact and uptake, in which the equilibrium of free Ag$^+$ and Ag(I) complexes may not be severely affected by the ligands in environmental surroundings.

Last but not least, it should be noted that Ag$_2$S/Ag^0 heterostructures, formed via the photoreduction of Ag$_2$S-NPs, have been reported to display synergetic toxic effects to E. coli K12 under light irradiation.[84] The observed synergetic bactericidal activity of this heterostructure could be attributed to enhanced formation of (i) surface ROS which is responsible for the collapse of cell walls and (ii) a closed intracellular circuit loop contributing to the release of lysates from the cells.[84] As such, in addition to consideration of the impact of silver transformation, speciation and longevity on the toxic effects, e$^-$/h$^+$ pair separation and ROS generation on photolysis of silver hetero-nanostructures should also be considered when examining the risks posed by Ag$_2$S-NPs entering the aquatic environment. Fig. 3 summarizes the possible environmental transformations of Ag$_2$S-NPs under light irradiation and the possible toxic effects associated with these transformations. Among the considerations above-mentioned, yet silver speciation should be in particular considered firstly, as speciation-dependent toxicity to organisms has been extensively demonstrated in previous studies; Ag$^+$ and/or Ag-NP would normally result in high acute toxicity compared to Ag$_2$S-NP, an important natural antidote of Ag-NP.[17] In general, either free or adsorbed Ag$^+$, regenerated Ag-NPs and residual Ag$_2$S-NPs would likely coexist in aqueous solutions, wherein for example, Ag$_2$S-NPs underwent transformation in the presence of

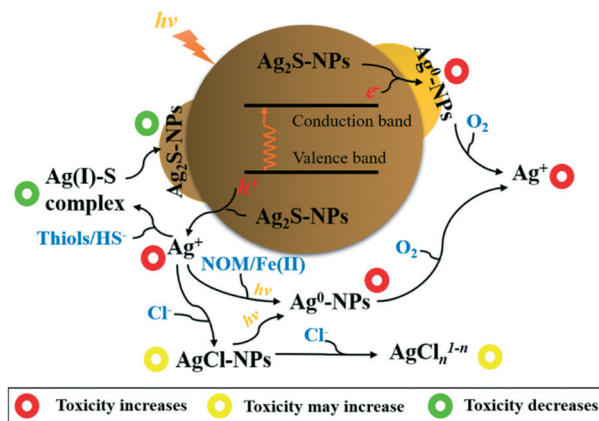**Fig. 3** Possible environmental transformation of Ag$_2$S-NPs and their associated toxic effects.

Fe(II) under light condition.[47] Speciation analysis of nano and ionic forms of silver has been developed and further applied to determine silver species in commercial products like an antiseptic kitchen cleansing spray.[97] Among available methods, collection and identification of Ag-NPs from aqueous solution with Ag-NPs and Ag$^+$ achieved through cloud point extraction-based separation, followed by the determination through graphite furnace atomic absorption spectroscopy.[98–100] Also, single-particle inductively coupled plasma mass spectrometry (ICP-MS) and ICP-MS coupled with size separation methods (e.g. capillary electrophoresis, hydrodynamic chromatography, field-flow fractionation and size-exclusion chromatography) have been able to directly identify and determine Ag-NPs in the mixture of Ag-NPs and Ag$^+$.[101–107] Nevertheless, methods are currently scarce for speciation analysis of Ag$^+$, Ag-NPs and/or AgCl-NPs and Ag$_2$S-NPs simultaneously, in particular separation and quantification of Ag-NPs from Ag$_2$S-NP solutions. Zhou et al. recently developed sequential elution and magnetic particles solid-phase extraction to achieve the speciation analysis of Ag$_2$S-NPs in environmental matrices with magnetic particles extraction of Ag-NPs, AgCl-NP and Ag$_2$S-NPs in the presence of Ag$^+$, firstly pre-eluting Ag-NPs and AgCl-NPs from matrices and then eluting Ag$_2$S-NPs followed by quantification of Ag$^+$ and/or Ag(I) complex by ICP-MS at elution interval, wherein low detection limit (0.068 μg L^{-1}) of Ag$_2$S-NPs was achieved.[106] Clearly, robust methods for speciation analysis of Ag$^+$, Ag-NPs, AgCl-NPs and Ag$_2$S-NPs in complex matrices were prerequisites for shedding light on the real risks of Ag$_2$S-NPs in the environment in order to achieve proper inclusions of environmental risks associated with Ag$_2$S-NPs.

5. Perspectives and outlook

The introduction of Ag-NPs into the environment is inevitable given the dramatic increase in the quantity of commercial products containing Ag-NPs entering daily life. Flow and mass balance models for Ag-NPs have shown that sulfidation of Ag-NPs occurs in urban sewage systems with the majority

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of the silver transferred on wastewater treatment to the sludge, which is then typically either landfilled, incinerated and/or used for agriculture. Nonetheless, a small percentage of Ag-NPs in the form of Ag_2S will remain in the WWTP effluent and enter natural aquatic environments. In this study, we have reviewed the formation, mobilization and redox transformation of Ag_2S-NPs in natural aqueous environments in the presence of various environmental constituents (including NOM, $Fe(III)/Fe(II)$, thiols/HS^-, Cl^-) with these transformations contributing to toxicity of silver in the environment. Although we start to understand how Ag_2S-NPs transform and how these transformations affect their toxicity, a few critical questions require to be answered for better understanding the environmental fate and impacts of Ag_2S-NPs in natural aquatic environments, including:

• Quantitative understanding of transformation mechanism of Ag_2S-NPs in natural aquatic environments.

Whilst a few studies reported to date provide some insight into the transformation mechanism of Ag_2S-NPs, quantitative understanding of the transformation of Ag_2S-NPs remains very limited. A preliminary mechanistically-based kinetic model (Fig. 1) consisting of a set of elementary reactions has been developed for the first time to describe the rate and extent of the photo-transformation of Ag_2S-NPs in the presence of $Fe(III)$ however there still exist many uncertainties for understanding of transformation behaviours of Ag_2S-NPs in natural aqueous environments. For example,

(i) it is undeniable that photo-Fenton reactions *via* the LMCT pathway may contribute to the oxidation of $S(-II)$ present in Ag_2S assemblages resulting in the release of Ag^+ under relatively acidic conditions, however these processes are unlikely to be important under most natural water conditions since Fe is mostly present as relatively non-photolabile iron oxides at typical natural water pHs. These processes are likely to be important in areas where receiving waters are impacted by acid discharge (*e.g.*, from acid mine drainage or acid sulfate soils runoff) which results in significantly lower pH conditions.[108] Hence, further work needs to be performed under environmentally relevant pH conditions and Fe concentrations to determine the importance of this process before incorporating the risks associated with these transformations on Ag toxicity.

(ii) The role separation of e^-/h^+ pairs under irradiation of Ag_2S-NPs in solubilization of Ag_2S-NPs is unclear. Although $Fe(III)$ may serve as an electron acceptor and enhance the separation of e^-/h^+ pairs and longevity of $h^+/\cdot OH$, its effect is expected to be negligible since the interaction of electrons with oxygen, which is present at much higher concentration in natural waters, appears to be more plausible.

(iii) Considering that chlorine and ozone can directly oxidize $S(-II)$ in Ag_2S-NPs leading to the release of Ag^+, can high-valent metal species (*e.g.* $U(VI)$ and $Mn(IV)$) solubilize Ag_2S-NPs? Although the standard reduction potential of the MnO_2/Mn^{2+} (+1.23 V) and $U(VI)/U(IV)$ (0.33 V) redox couples are higher than the reduction potential of the SO_4^{2-}/S^{2-} redox couple (−0.22 V) with these values supporting the hypothesis that the oxidation of Ag_2S is thermodynamically feasible in the presence of $U(VI)$ and/or $Mn(IV)$ under standard condition, the feasibility as well as the kinetics of these reactions at environmentally relevant conditions are still not known. Further investigations focusing on the effect of redox-active metal species on mobilization of Ag_2S-NPs are urgently required.

(iv) Given that both Fenton/Fenton-like reactions and the disproportionation of $O_2^{\cdot-}$ are strongly pH dependent and both NOM and Cl^- are capable of mediating the variation of Ag speciation, developing an understanding of the impact of these environmental factors on the mobilization of Ag_2S-NPs and incorporating these factors in the kinetic model is critical to fully evaluating the transformation behaviour of Ag_2S-NPs in natural environmental conditions.

Most of the studies on interactions of Ag_2S-NPs and environmental matrices have been undertaken at relatively high concentrations. However, investigation of transformation of Ag_2S-NPs at much lower (and more realistic) concentrations are rare. Although state-of-the-art ICP-MS may be capable of detecting trace amounts of Ag species, challenges remain with regard to the complexity of determining the concentrations of each silver species in more realistic environments. The kinetic modelling approach described here enables the construction of mechanistically-based mathematical models based on a hypothesized reaction set and appropriate rate constants potentially provides the capacity to predict the transformation behaviour of Ag_2S-NPs under realistic aquatic environments.

• Assessing effects of transformation of Ag_2S-NPs on toxicity.

Previous studies have shown that sulfidation of Ag-NPs can effectively reduce toxicity. However, the ease with which Ag_2S-NPs may transform in some environments leading to the initial rapid release of dissolved $Ag(I)$ and subsequent formation of Ag^0-NPs suggests that Ag_2S-NP safety may be overestimated in some cases. In addition, formation of Ag^0/Ag_2S hetero-nanostructures exhibiting enhanced charge separation may lead to ROS production at cell surfaces with subsequent lysis of cells following direct contact. In complex natural environments, other sulfurized metals (such as ZnS, FeS and CdS) may be formed through cation exchange reactions between metal ions and Ag_2S and how these semiconductors contribute to the separation of e^-/h^+ pairs in the resulting heterostructures and affect the toxicity of these composite systems is unknown. Therefore, *in vitro* and *in vivo* experiments following exposure of these transformed Ag_2S-NPs (*e.g.* Ag_2S-based hetero-nanostructures) to the various organisms are required to fully understand the acute toxicity of Ag_2S-NPs in natural environments.

• Identifying the bioaccumulation pathway of Ag_2S-NPs and contribution of bioaccumulation to chronic toxic effects.

Debate exists as to whether intact Ag-NPs or soluble Ag^+ are taken up by organisms. Although a few studies have provided evidence of "direct" uptake of Ag-NPs and Ag_2S-NPs with these particles directly analysed or visualized within organisms,[20–22,109,110] it remains unclear whether a soluble

Ag$^+$ form is taken up with subsequent formation of NPs within organisms. Indeed, following exposure of plants to Ag$^+$, the reduction of Ag$^+$ to form metallic Ag-NPs and the formation of Ag$_2$S-NPs *via* sulfidation with HS$^-$/thiols in organism were observed.[22,111,112] Debate also exists concerning whether sulfidation reduces or increases the bioavailability of AgNPs. On one hand, sulfidation of Ag-NPs reduced their bioavailability, resulting in significant decrease in the bioaccumulation of Ag-NPs.[20,110,113] On the other hand, the accumulation of silver was observed to be higher in both *Daphnia magna* and rainbow trout exposed to Ag(I) in the presence of sulfide than that in its absence.[114,115] Although exposure to Ag$_2$S-NPs may not result in acute toxic effects, it may lead to chronic yet sublethal toxic effects as a result of the accumulation of Ag$_2$S-NPs in aquatic organisms. Therefore, studies on chronic toxicity of Ag$_2$S-NPs to different organisms and understanding the relationship between bioaccumulation and chronic toxic effects of Ag$_2$S-NPs is needed in order to fully examine the long-term risks of Ag$_2$S-NPs in the aqueous environment.

Conflicts of interest

The authors declare no competing financial interest.

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