Formation of Nanosilver from Silver Sulfide Nanoparticles in Natural Waters by Photoinduced Fe(II, III) Redox Cycling

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S Supporting Information

ABSTRACT: Nanosilver (nAg) has been repeatedly demonstrated to end up as silver sulfide nanoparticles (Ag₂SNPs), but little is known about the potential transformations of Ag₂SNPs in natural environments that are very important for comprehensive assessments of nAg risks to human and environmental health. Here we show that Ag₂SNPs can release tiny amounts of silver ion via cation exchange reactions between Ag(I) and Fe(III) in the dark, while in the light dramatic dissolution of Ag₂SNP occurs, which is mainly attributed to the Ag₂SNP oxidation by the hydroxyl radical formed during the reduction of Fe(III) to Fe(II) in water under sunlit conditions. However, silver ions are subsequently reduced to nAg in the light due to the strong reducing power of Fe(II). Thus, the formation of nAg from Ag₂SNPs in the presence of Fe(III) under light conditions proceeds through a two-step reaction mechanism, the photoinduced and Fe(III)-dependent dissolution of Ag₂SNPs, followed by the reduction of silver ions to nAg by Fe(II). The formation of nAg from Ag₂SNPs is also validated in environmental waters under light conditions. It is thus concluded that photoinduced Fe(III)/Fe(II) redox cycling can drive the formation of nAg from Ag₂SNPs in natural waters. These findings suggest that the previous consensus about the stability of Ag₂SNPs in aquatic environments should be reconsidered.

INTRODUCTION

Nanosilver (nAg) is being widely used in commercial products, which can release nAg to the environment during the manufacturing, use and disposal of these products.^{1–3} nAg has been shown to readily undergo sulfidation,^{4–9} which transforms nAg to highly insoluble and stable silver sulfide nanoparticles (Ag₂SNPs),^{10–13} reducing the toxicity of nAg to organisms such as *Escherichia coli*,¹⁴ least duckweed, nematode worm, zebrafish, and killifish.^{14,15} Consequently, there is an emerging consensus that the use of nAg is unlikely to impose risks on human and environmental health due to the existence of sulfidation as a natural and ultimate antidote.^{10–19} Given precautionary principles, however, some uncertainties remain as follow: Are they truly stable? Can silver be remobilized from Ag₂SNPs under environmental conditions? If so, how can transformations of Ag₂SNPs occur in natural environments? These concerns are very important for scientists to fully understand the risks of nAg to human and environmental health.

Ag₂SNPs were reported to be chemically stable and have profoundly low silver lability over an incubation period of several months in soils or composting sludge.^{10–13,16} However, a recent study showed that rapid oxidation of Ag₂SNP can occur in wastewater effluent treated by ozone, along with the

release of silver ions and particularly a change in species, resulting in an increase in their acute toxicity to green algae.²⁰ Our study has shown that light irradiation also influences the stability of Ag₂SNPs in water containing Fe(III),²¹ indicating that light and Fe(III) probably have the potential to drive Ag₂SNPs transformations. Nevertheless, the potential pathways and mechanisms for the transformations of Ag₂SNPs in natural waters are unknown, representing an uncertainty of their risks to the environment and, on a larger scale, to human health.

Herein we fully investigate the pathway and mechanism for transformations of Ag₂SNPs in water with an environmentally relevant concentration of Fe(III) under both light and dark conditions. We propose that the transformation of Ag₂SNPs in the presence of Fe(III) under light conditions proceeds through a two-step reaction mechanism, the photoinduced and Fe(III)-dependent oxidation of Ag₂SNP, followed by the reduction of silver ions to nAg by Fe(II). We further exploit this mechanism in natural waters including landscape water, wastewater treatment plant effluent and river water, confirming

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that the formation of nAg from Ag₂SNPs can indeed occur. Our findings suggest that the previous consensus about the stability of Ag₂SNPs in aquatic environments should be reconsidered.

MATERIALS AND METHODS

Materials. In the present study, the reagents except for the solid isotope Ag¹⁰⁷ were purchased from Sigma-Aldrich. The Ag¹⁰⁷ (99%) was from Trace Sciences International (Delaware, USA), and it was dissolved by guaranteed reagent nitrate acid in an ultrasonic bath (KQ-600E, 40 kHz, 600 W) for 4 h, followed by dilution with ultrapure water for Ag¹⁰⁷NO₃ preparation. The Ag₂SNPs (34–91 nm) with average size of 57.2 ± 5.3 nm were prepared by the reaction of AgNO₃ with elemental sulfur, which has been shown in our previous study.²¹ Briefly, 7.1 mg sulfur, dissolved in 10 mL warm ethanol (~60 °C), was added dropwise to AgNO₃ solution (50 mL, 170 mg/L) with 10 mg PVP-40. The reaction was kept for 5 h at 95 °C under dark conditions, with a water-cooling system. The Ag₂SNPs suspension was purified with five cycles of washing with ultrapure water using centrifugation (9384g, 30 min), concentrated to approximately 150 mg/L and stored at 4 °C in the dark for later use. The Ag₂¹⁰⁷SNPs, using Ag¹⁰⁷NO₃ as a precursor, were prepared using the above-mentioned process as well.

Characterization Analysis of NPs. The morphology of NPs in this study was observed on a JEOL JEM-2100F high-resolution transmission electron microscope (HRTEM) at 200 kV, and the elemental mapping of the imaged objects was characterized using an EDS detector (Oxford Inca, UK). The HRTEM samples were prepared by depositing 20 µL aliquots of aqueous sample on the ultrathin carbon-coated copper grids, followed by drying in a vacuum desiccator. The silver ions collected with centrifugal filtration (Amicon Ultra-15, 3kD) at 9384 g for 15 min, were quantified using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 8800, USA). The XRD pattern of samples was measured by using a PANalytical X'Pert PRO diffractometer with Cu Kα radiation (λ = 0.154 nm), with the diffraction angle (2θ) from 10° to 90° at 0.0263° per step. The NPs for XRD analysis were separated from solution by using centrifugal ultrafiltration (Amicon Ultra-15, 3kD) and the pellet was precipitated dropwise on a glass slide, followed by drying in a vacuum desiccator. The surface morphologies of bulk Ag₂S particles were characterized on a Hitachi SU8020 FESEM at 3 kV acceleration voltage and 5.2 mm working distance.

Transformations of Ag₂SNPs under Simulated Light. The transformations of Ag₂SNPs in the presence of Fe(III) were performed under simulated light and in the dark, respectively. The experiments using simulated light exposure were conducted in a solar simulator with three air-cooled 2500 W Xe lamps (SN-500, Beifang Lihui, China). Quartz glass bottles (100 mL) with quartz caps were used in this study. The dark control experiment was performed in quartz glass bottles wrapped by four layers of aluminum foil and placed in the same solar simulator. The intensity of simulated light was set at 550 W/m², and the temperature was kept at 36 ± 2 °C by using an air-cooling system. The Ag₂SNPs stock solution was diluted by using 5 mM borate buffer, followed by the addition of Fe(III) stock solution (100 mg/L) which was prepared by dissolving Fe(NO₃)₃·9H₂O in 2 mM HNO₃, yielding a mixture of 5 mg/L Ag₂SNPs and 2 mg/L Fe(III). At each time interval (0, 4, 10, 18, 24, 48, 72, and 96 h), a 10 mL aliquot of aqueous sample was taken from each quartz glass bottle. It should be noted that

the solution was stirred to ensure homogeneity before sample collection. Centrifugal ultrafiltration (Ultra-15, 3kD, Millipore, MA) at 9384g for 15 min was used to collect the silver ions released from Ag₂SNPs,¹⁵ and pellets were collected for identification of particles by characterization analysis. The recovery efficiency of 1 mg/L AgNO₃ solution is 94.1 ± 2.2%, suggesting negligible loss of the analyte during the centrifugal ultrafiltration. All experiments were performed in triplicate.

Transformations of Ag₂SNPs under Natural Sunlight.

For experiments under natural sunlight, quartz glass bottles containing a mixture of 5 mg/L Ag₂SNPs and 2 mg/L Fe(III) were placed in front of Building No. 3 in the Research Center for Eco-Environmental Sciences (40°00'26.94"N, 116°20'15.10"E), Chinese Academy of Sciences, Beijing, from the first to the eighth of July 2015 when it is continuously sunny, with a temperature between 18 and 34 °C. The exposure to sunlight began near midday (11:00 a.m.) on July first. A total of 4 mL of aqueous sample was taken at 19:00 (the time of sundown in summer in Beijing) on July first, 5:00 (the time of sunrise in summer in Beijing) and 19:00 on July second, 5:00 and 9:00 on July third, 11:00 on July fourth, 12:00 noon on July fifth, 10:00 on July sixth, 11:00 on July seventh, and 11:00 on July eighth. Centrifugal ultrafiltration (Ultra-4, 3kD, Millipore, MA) at 9384g for 15 min was used to collect silver ions released from the Ag₂SNPs,¹⁵ and pellets were collected for identification of particles by characterization analysis. All experiments were performed in triplicate.

Formation of nAg from Ag₂SNPs in Natural Waters.

Environmental water samples including landscape water, wastewater treatment plant effluent and river water were collected in Beijing by using polyvinyl chloride (PVC) containers (2.5 L), and all containers were rinsed 3-fold with the sample before they were filled up to volume. Samples were filtered through a 0.45 µm glass fiber filter (Pall Corporation, MI) and then spiked by stock Ag₂SNPs and Fe(III), leading to concentrations of 5 mg/L and 2 mg/L, respectively. Afterward, the samples were exposed to the light. Ten mL of sample was taken from each quartz glass bottle for identification of particles by characterization analysis.

Effect of Radical Scavengers on the Dissolution of Ag₂SNPs. To confirm the contribution of hydroxyl radical to photoinduced dissolution of Ag₂SNPs in the presence of Fe(III), effects of radical scavengers such as tertiary butyl alcohol (TBA) and catalase on the Ag₂SNPs dissolution were investigated. A catalase stock solution (1000 U/mL) from bovine liver or TBA (20 mM) was added to the mixture of Ag₂SNPs (5 mg/L) and Fe(III) (2 mg/L) to yield 300 U/mL catalase or 2 mM TBA, respectively. These samples were exposed to the simulated light for 96 h, and the samples were collected at 0, 4, 6, 10, 24, 48, 72, and 96 h, respectively, followed by determination of silver ions using ICP-MS.

Evidence for Formation of nAg from Ag₂SNPs. As the separation of low concentrations of nAg from Ag₂SNPs is challenging, the mixture of Fe(III) and Ag₂SNPs exposed to simulated light and in the dark for different time periods was ultracentrifuged (3 kDa, 15 min, 9384g), respectively, and the pellet was washed with ultrapure water, followed by ultracentrifugation (3 kDa, 15 min, 9384g) again to remove all remaining silver ions. Afterward, the purified pellet was incubated in 10 mM H₂O₂ for 20 min to dissolve silver particles,^{22,23} and then the solution was ultracentrifuged (3 kDa, 15 min, 9384g) to collect the ultrafiltrate for ICP-MS measurements. The results of ICP-MS indicate the amount of

Figure 1. Kinetics of Ag₂SNPs transformation in borate solution without or with Fe(III) under light and in the dark, respectively. (A) Dissolution kinetics of Ag₂SNPs, and inset is the amplification of the sample with Fe(III) in the dark. (B) Time-resolved concentrations of Fe(II) in the Ag₂SNPs solution. Fe(II) is considered as the product of Fe(III) reduction when Ag₂SNPs dissolution occurs under lighted conditions. (C) Time-resolved concentrations of SO₄²⁻ in the Ag₂SNPs solution. The occurrence of SO₄²⁻ is observed in Ag₂SNPs solution with Fe(III) under light conditions.

partial nAg which was dissolved by the 10 mM H₂O₂ during the period of 20 min.

On the other hand, the ratio of Ag¹⁰⁷ to Ag¹⁰⁹ was investigated by using a mixture of commercial AgNPs (1 mg/L) and the synthesized Ag₂¹⁰⁷SNPs (5 mg/L) in the presence of Fe(III) (2 mg/L) under light conditions. The mixture was exposed to the simulated sunlight and 10 mL samples were collected at 0, 4, 10, 24, 48, 72, and 96 h, respectively. The samples were pretreated using the above-described method and the ultrafiltrates were measured by using ICP-MS.²⁴ The value of the ratio of Ag¹⁰⁷/Ag¹⁰⁹ was calculated through comparison between counts per second (cps) of Ag¹⁰⁷ and that of Ag¹⁰⁹.

RESULTS AND DISCUSSION

Fe(III)-Dependent Dissolution of Ag₂SNPs. The time-resolved concentration of silver ions is highly dependent on the occurrence of Fe(III) (Figure 1A); dissolution of Ag₂SNPs is negligible in the absence of Fe(III) under light conditions or in the dark, while measurable concentrations of silver ions are observed in the Ag₂SNPs solution with an environmentally relevant concentration of Fe(III) under both light and dark conditions. It is evident that Fe(III), one of the most abundant metals in terrestrial and aquatic environments, is a key factor controlling the dissolution of Ag₂SNPs. In the presence of

Fe(III), the amount of release of silver ion from Ag₂SNPs under light irradiation (~4.1%) is an order of magnitude greater than that in the dark (~0.16%), indicating that light irradiation dramatically enhances the Ag₂SNPs dissolution. Also, the concentration of silver ions remains constant after a small initial increase within the first 4 h in the dark, while a rapid increase within the first 4 h followed by a continuous decrease of silver ions for the next 20 h is observed in the light. This suggests that different pathways and mechanisms contribute to the Ag₂SNPs dissolution process in the presence of Fe(III) depending on whether it occurs in the light or dark mode. Previous studies have already predicted potential dissolution of Ag₂SNPs in the natural environment,^{25,26} although Ag₂S is considered as one of the most insoluble minerals. Here our findings demonstrated that Ag₂SNPs could undergo dissolution in the water with an environmentally relevant concentration of Fe(III).

Sulfate, as well as Fe(II), the product of Fe(III) reduction, are detected under light conditions (Figure 1B,C). Given the thermodynamics of Ag and Ag₂SO₄, it was possible for the occurrence of Ag₂SO₄ when both Ag⁺ and SO₄²⁻ were simultaneously present in the solution. As shown in Figure 1A and B, comparable trends between silver ions and Fe(II) kinetics are observed. Both silver ions and Fe(II) reach highest levels at 4 h, followed by continuous decreases until 24 h

Figure 2. Role of hydroxyl radical on the dissolution of Ag_2SNPs with Fe(III) under simulated light. (A) Time-resolved hydroxyl radical ESR signal (DMPO spin trap) induced by the mixture of Ag_2SNPs and Fe(III) in the light. Note that 100 mM DMPO in ultrapure water was used in this study. (B) Effect of radical scavengers on the dissolution of Ag_2SNPs .

elapsed. It is therefore assumed that the dramatic increase of silver ions in the light is related to the oxidation of Ag_2SNP . A recent publication reported that O_3 -induced Ag_2SNP oxidation occurred in wastewater treatment plant effluent, where the release of silver ions and sulfate formation were observed.²⁰ The hydroxyl radical, a powerful oxidant, can be generated during the reduction of Fe(III) to Fe(II) in the presence of light,^{27,28} which is confirmed through the stable spin adduct formed with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) (Figure 2A). The level of the hydroxyl radical remains constant after a rapid decrease within the first 4 h, which corresponds well to the rapid increase of silver ions and Fe(II) during the first 4 h in the light. Clearly, the hydroxyl radical likely contributes to the dramatic increase in silver ions under light conditions.

To further confirm whether the hydroxyl radical is the contributing factor to the dissolution of Ag_2SNPs in the light, radical scavengers such as TBA or catalase were added to the Ag_2SNPs solution. The Ag_2SNPs dissolution is significantly inhibited after addition of TBA or catalase in the light (Figure 2B). The release of silver ions decreased from $\sim 4.1\%$ to $\sim 1.1\%$ when 2 mM TBA was added to the Ag_2SNPs solution, demonstrating that hydroxyl radical-based oxidation of Ag_2SNP contributes to the dissolution of Ag_2SNP in the presence of Fe(III) under light conditions. Moreover, catalase completely inhibits the Ag_2SNPs dissolution in the presence of Fe(III) even under light conditions (Figure 2B). On account of these observations, we believe that the dramatic increase of silver ions in the light is mainly attributed to the oxidation of Ag_2SNP due to the active hydroxyl radical formed during the reduction of Fe(III) to Fe(II) in water under light irradiation.

In the dark, however, we find the negligible effect of catalase on the dissolution of Ag_2SNPs in the presence of Fe(III) (Figure S1). Moreover, given the negligible levels of Fe(II) and sulfate (Figure 1B,C), we postulate that cation exchange reactions (CERs)^{29–31} instead of the oxidation pathway may contribute to the occurrence of measurable silver ions in the dark. Exchange reactions between metallic ions and metal sulfides can occur due to the great differences in solubility of different metal sulfides.^{3,5,32,33} Indeed, both Fe(III) and Hg(II) can rapidly react and displace Ag(I) from Ag_2SNPs (Figure S2)

due to the much lower K_{sp} values of Fe_2S_3 (1.4×10^{-88}) and HgS (2×10^{-53}) than that of Ag_2S ($K_{\text{sp}} = 8 \times 10^{-51}$), resulting in the occurrence of measurable silver ions in the dark. In contrast, the dissolution of Ag_2SNPs in the presence of Cu(II) or Pb(II) is negligible under dark conditions (Figure S2). This is understandable given the higher solubility of CuS ($K_{\text{sp}} = 8 \times 10^{-37}$) and PbS ($K_{\text{sp}} = 3 \times 10^{-28}$) than that of Ag_2S . These results suggest that the CER between Ag(I) and Fe(III) is a potential mechanism for the Fe(III) -dependent dissolution of Ag_2SNPs in the dark. Moreover, the increase in the release of silver ions from Ag_2SNPs follow first order kinetics with rate constant (k) of 1.06 h^{-1} (Figure S3).

Formation of nAg in the Light. Given the strong reducing capacity of Fe(II) and the comparable trend between silver ions and Fe(II) kinetics (Figure 1A,B), we postulate that the formation of nAg particles may contribute to the decrease in silver ions under light conditions. This assumption is validated by the observation of nAg particles between 15 and 30 nm in size in the Ag_2SNPs solution after 24 h of light irradiation. The occurrence of nAg is clearly evidenced through the results of high resolution transmission electron microscopy (HRTEM) and energy-dispersive spectroscopy (EDS) (Figure 3A–D). The lattice fringe spacing of $\sim 2.02 \text{ \AA}$ is observed in the HRTEM image (Figure 3A), which corresponds to the {200} plane of silver.^{34,35} Also, we examine the feasibility of nAg formation through the reaction between silver ions and Fe(II) in the light. Visible changes include the occurrence of silvery colloidal particles occur within 48 h in the light after mixing the silver nitrate and Fe(II) . Moreover, both HRTEM-EDS analysis and the XRD spectrum provide robust evidence that silver ions are indeed able to be reduced to nAg by Fe(II) in the light (Figure S4).

We further performed silver isotope (Ag^{107}) experiments to examine the formation of nAg from Ag_2SNPs under light conditions. According to previous studies, introduction of diluted H_2O_2 (10 mM) can effectively oxidize nAg to silver ions, while Ag_2S particles remain unchanged.^{22,23} As shown in Figure 4A, the mass of nAg dissolved by 10 mM H_2O_2 gradually increases from 0 to $6.8 \mu\text{g}$ during the first 24 h, after which little further increase occurs in the light, while there is no increase during the whole experimental time under dark conditions. It is

Figure 3. Identification of NPs after transformations of Ag_2SNPs in borate solution with an environmentally relevant concentration of Fe(III) under simulated light. (A) TEM image. (B) HRTEM image of nAg with a lattice spacing of 2.02 Å. (C–E) EDS elemental mappings of the NPs after chemical transformations of Ag_2SNPs .

clear that nAg particles indeed form in the Ag_2SNPs solution with Fe(III) under light conditions. On the other hand, the ratio of Ag^{107} to Ag^{109} , calculated using their counts per second (cps) values from the inductively coupled plasma mass spectrometry (ICP-MS) measurements, maintains an equilibrium after a rapid increase by 2.6 ± 0.9 during the first 24 h in the light (Figure 4B). However, a negligible increase is observed during 96 h for the pure commercial nAg ($\text{Ag}^{107}/\text{Ag}^{109}$ ratio: 1.07^{36,37}) (Figure 4B). This finding demonstrates the occurrence of nAg¹⁰⁷ in the solution containing both $\text{Ag}_2^{107}\text{SNPs}$ and commercial AgNPs under light conditions. Also, the Ag^{107} of nAg¹⁰⁷ derives from the $\text{Ag}_2^{107}\text{SNPs}$, so this provides robust evidence for the formation of nAg from Ag_2SNPs in the presence of Fe(III) in the light.

We also found that these new AgNPs formed probably would not be oxidized back to Ag^+ even in the light for long time. As shown in Figure S5, it is evident that Ag^+ concentration increased within the first 4 h followed by a decrease for the next

20 h, and then the Ag^+ level remains constant for the next 268 h. This might be attributed to the stabilization of iron coating adsorbed on the surface of these new AgNPs, which could be observed in the HRTEM images (Figure 3). However, the concentration of Ag^+ would rapidly increased again when we added a second equivalent of Fe(III) to the solution, demonstrating the great role of Fe(III) in the transformation of Ag_2SNPs in water.

Transformations of Ag_2SNPs in Natural Sunlight. The transformations of Ag_2SNPs were examined in the presence of Fe(III) under natural sunlight. Figure S6 shows the dissolution kinetics of Ag_2SNPs in borate solution with an environmentally relevant concentration of Fe(III) under sunlight. The results indicated that the dissolution of Ag_2SNPs in the presence of Fe(III) can indeed occur in the daytime, while the concentration of silver ions remains constant in the night (Figure S6). This agrees well with the results observed in the laboratory. The extent of Ag_2SNPs dissolution under natural

Figure 4. Evidence supports the formation of silver particles from Ag_2 SNPs in the presence of Fe(III) under lighted conditions. (A) Measured mass of silver particles dissolved with 10 mM H_2O_2 at room temperature for 20 min. (B) The change in time-resolved Ag^{107}/Ag^{109} of commercial AgNPs (1 mg/L) and commercial AgNPs (1 mg/L) with synthesized Ag_2^{107} SNPs (5 mg/L) in the presence of Fe(III) (2 mg/L) under lighted conditions, respectively. The value of Ag^{107}/Ag^{109} is calculated through comparison between counts per second (cps) of Ag^{107} and those of Ag^{109} , and the $\Delta(Ag^{107}/Ag^{109})$ shown is obtained through subtraction of the value of Ag^{107}/Ag^{109} at 0 h.

sunlight is $\sim 10.9\%$, being far greater than that under simulated light in the laboratory. This significant difference can likely be attributed to the role of ultraviolet light; compared containers made of quartz glass, the extent of dissolution of Ag_2 SNPs in normal glass bottles is clearly low under natural sunlight (Figure S7).

The HRTEM and EDS elemental mapping analysis confirm the presence of nAg in the Ag_2 SNPs solution containing an environmentally relevant concentration of Fe(III) under natural sunlight conditions (Figure S8), documenting the potential formation of nAg from Ag_2 SNPs in the ambient environment.

Formation of nAg from Ag_2 SNPs in Natural Waters. The formation of nAg from Ag_2 SNPs is further examined by using natural waters such as landscape water, wastewater treatment plant effluent and river water. Here the formation of nAg particles is evidenced through the HRTEM and EDS (Figure 5 and Figures S9, S10). Clearly, these results indicate that photoinduced formation of nAg from Ag_2 SNPs in the presence of Fe(III) may occur widely in aquatic environments,

suggesting a potential natural source of nAg in the nature environment. Measurable Fe(III) have been reported in some surface waters,^{38,39} so the formation of nAg from Ag_2 SNPs must be taken into account when considering the fate of nAg in natural environments.

Pathway of Fe(III)-Dependent Transformations of Ag_2 SNPs in Water. Figure 6 summarizes the potential pathway of Fe(III)-dependent transformations of Ag_2 SNPs in water. In the light, hydroxyl radical can be generated during the reduction of Fe(III) to Fe(II) in water,^{27,28} mainly contributing to the significant release of silver ions from Ag_2 SNPs. The silver ions thus released are gradually reduced to nAg by Fe(II). These combined results allow us to propose that the formation of nAg from Ag_2 SNPs in the presence of Fe(III) under light conditions may proceed through a two-step reaction mechanism, the photoinduced and Fe(III)-dependent dissolution of Ag_2 SNPs, followed by the reduction of silver ions to nAg by Fe(II) (eqs 1-3).

The photoreduction of Fe(III) (eq 1) in the light produces the hydroxyl radical,^{27,40,41} which enables the dissolution of Ag_2 SNPs and generation of sulfate (eq 2),^{42,43} along with a remarkable decrease in dissolved oxygen (Figure S11). The silver ions are reduced to nAg by Fe(II) in the light (eq 3). These results provide robust evidence to support the proposed reaction mechanism that photoinduced Fe(II, III) redox cycling drives the formation of nAg from Ag_2 SNPs in water.

In the dark, we propose that silver is remobilized from Ag_2 SNPs through the CER between Fe(III) and Ag(I) of Ag_2 SNPs. Its pathway is not currently understood, but may be related to the formation of Fe_2S_3 that tends to be unstable and decomposes to FeS,^{42,44} followed by the second CER between FeS and the released silver ions to reform Ag_2 SNPs.²¹ When the CERs maintain an equilibrium within a short time, the concentration of silver ions remains constant.

Environmental Implications. Previous studies have already shown that dissolved silver mainly controls the toxicity of particles containing silver to organisms.^{15,45} Our findings suggest that Ag_2 SNPs safety may be overestimated in past studies, even though the released silver ions subsequently decrease due to the formation of nAg. The rapid increase of silver ions release from Ag_2 SNPs during the initial stage of light exposure indicates that acute toxicity of Ag_2 SNPs in Fe(III)-present environments may occur. The transformation processes especially dissolution, therefore, potentially affect the hazard of Ag_2 SNPs, which should be taken into account when assessing their risks to aquatic ecosystems. In general, Ag_2 SNPs are mainly in sludge of wastewater treatment plant.²⁵ The main pathway by which Ag_2 SNPs enter natural environment is via application of sludge to soils, since erosion could release Ag_2 SNPs to stream, rivers and lakes. A buildup of Ag_2 SNPs in surface waters will raise concern about their potential hazards associated with transformations.

Our findings provide information for further understanding the environmental fate of nAg as well as for discovering a potential source of naturally occurring nAg in aquatic environment. The nAg particles, formed from Ag_2 SNPs, show

Figure 5. HRTEM images of NPs after transformations of Ag_2SNPs in landscape water with Fe(III) under light. (A) HRTEM image. (B) nAg with a lattice spacing of 2.07 Å. (C) EDS image of the nAg particle in (B), and the presence of Cu peaks is attributed to the ultrathin carbon-coated copper grids for HRTEM analysis. (D–F) EDS elemental mappings of the nAg shown in Figure 4B.

Figure 6. Pictorial summary of the proposed pathway of Fe(III) -dependent transformations of Ag_2SNPs in water.

far smaller size than Ag_2SPs , which will inevitably influence their transport in the natural environments, as previous study has shown that coexisted particles can influence behavior of NPs.^{46,47} Moreover, the nAg can likely deliver much farther distances in the natural environments, since a recent study documented that small particles always show greater mobility than big particles.⁴⁸ Taken together, the real risks of Ag_2SNPs in natural waters must be more comprehensively re-evaluated in future studies, especially for the hazard of forming nAg particles.

■ ASSOCIATED CONTENT

§ Supporting Information

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Additional details of results (PDF)

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Notes

The authors declare no competing financial interest.

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