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Transformation kinetics of silver nanoparticles and silver ions in aquatic environments revealed by double stable isotope labeling†

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Silver nanoparticles (AgNPs) are rather mutable in water columns, and the oxidation of AgNPs to release Ag⁺ and reduction of Ag⁺ to regenerate AgNPs exist simultaneously in certain environments, making it rather difficult to monitor the reaction kinetics. In this study, we synthesized isotopically labeled AgNPs (99.5% ¹⁰⁷Ag, ¹⁰⁷AgNPs) and AgNO₃ (99.81% ¹⁰⁹Ag, ¹⁰⁹AgNO₃). For the first time, two stable Ag isotopes were used in the same experiment to track the transformation kinetics of AgNPs and Ag⁺ independently in aquatic environments. It was found that the oxidation of AgNPs dominated the reaction in simple water solutions containing both ¹⁰⁷AgNPs and ¹⁰⁹Ag⁺. Sunlight significantly accelerated the dissolution of the ¹⁰⁷AgNPs, but longer solar irradiation (8 h) triggered aggregation of the ¹⁰⁷AgNPs and therefore reduced the reaction rate. With the addition of 5 mg C L⁻¹ dissolved organic matter, the reduction of ¹⁰⁹Ag⁺ played the leading role. The corrected concentration of dissolved ¹⁰⁷Ag⁺ began to decrease after some time, indicating other reduction mechanisms were happening. An elevated pH (pH 8.5) could even completely inhibit the oxidation of ¹⁰⁷AgNPs. All the reactions seemed stalled at low temperature (6 °C) except the dissolution of ¹⁰⁷AgNPs under solar irradiation, suggesting a non-negligible effect of sunlight. The presence of divalent cations induced agglomeration of ¹⁰⁷AgNPs, but the reduction of ¹⁰⁹Ag⁺ was not significantly affected. These findings implied that the transformation between AgNPs and Ag⁺ was rather complex and greatly depended on the external conditions. Given the fact that Ag⁺ has been shown to be much more toxic than AgNPs, the speciation change may dramatically impact the final toxicity and bioavailability of AgNPs, so there is a high demand for assessing the environmental risks of AgNPs under more realistic conditions.

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Nano impact

With the ongoing commercialization of silver nanoparticles (AgNPs), their release to the environment will increase considerably. AgNPs are highly dynamic, and the fate of AgNPs in aquatic systems is still largely unknown, especially the transformation between AgNPs and Ag⁺, which remains a bottleneck in rationally estimating their potential risks. In this study, a double stable isotope labeling method was used to monitor the transformation kinetics of AgNPs and Ag⁺ in aquatic environments. It was demonstrated that transformation between AgNPs and Ag⁺ was complicated, and was affected by a number of environmental factors such as sunlight, dissolved organic matter, solution pH, temperature, and divalent cations. The speciation variation of silver may significantly impact the toxicity and bioavailability of AgNPs. Therefore, more realistic conditions are highly necessary when assessing the environmental hazards of AgNPs.

1. Introduction

Due to their excellent optical, electrical, catalytic and antimicrobial properties, silver nanoparticles (AgNPs) can find applications in a range of industrial processes and medical fields. Their superior antibacterial ability also encourages

their use as constituents in an increasing range of daily consumer goods.¹ However, during the production, usage and disposal of these products, AgNPs would inevitably be released into natural systems, which raises particular concerns over their complicated interactions with the biosphere and the adverse ecological effects.^{2–5}

The physical state and chemical form of nanoparticles (NPs) should be specially considered as they greatly affect the final fate, transport and related toxicity of NPs within natural systems.⁶ AgNPs are far from environmentally inert, and once released into water, multiple chemical and physical transformations are expected to occur, such as aggregation,

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oxidation, dissolution and sulfidation,⁷ of which the initial oxidation is regarded to be of ultimate importance, partially because it is the first step for AgNPs to react with reduced sulfur and chloride.⁸ More importantly, the oxidation of AgNPs to release Ag⁺ can significantly alter the potential toxicity and bioavailability of Ag from AgNPs.^{9–11} The dissolution of AgNPs is a cooperative oxidation process involving both dissolved oxygen and protons,¹² and peroxide intermediates were produced *via* the oxidation of AgNPs by oxygen.^{13–15} Other properties of AgNPs such as the particle size, shape, and surface coating,^{16–19} and the surrounding variables including the solution ionic strength, specific ligands, and natural organic matter (NOM) could also greatly affect the behavior of AgNPs.¹² On the other hand, because of the modest redox potential of silver ($\varphi^0\text{Ag}^+/\text{Ag}^0 = 0.80\text{ V}$), Ag⁺ can also be reduced to AgNPs by some reducing agents in the environment, such as the omnipresent dissolved organic matter (DOM). A myriad of functional groups, including phenolic-OH, quinones, hydroxyl groups, and ketones, contained in DOM create a perfect reductive environment for the reduction of Ag⁺, and the DOM related formation of AgNPs has been extensively reported. Humic acid (HA) and fulvic acid (FA) of different origins could drive the generation of AgNPs under environmentally relevant conditions, and the reduction kinetics of Ag⁺ was enhanced considerably at elevated temperature and pH.^{20,21} Sunlight was reported to accelerate the reduction of Ag⁺, and superoxides generated from the solar irradiation of phenol groups in DOM were involved in the reduction.^{22,23} Moreover, the reconstitution of AgNPs from bulk objects was also observed under ambient conditions at a relative humidity higher than 50%, revealing the mutable nature of AgNPs.^{24,25}

Our previous study demonstrated that AgNPs are highly dynamic in certain aquatic environments, and the release of Ag⁺ by oxidation of AgNPs and regeneration of AgNPs smaller than the primary NPs by reduction of Ag⁺ could both occur in sunlit DOM-rich water.²⁶ Due to the different environmental behaviors of AgNPs and Ag⁺ in aquatic systems and their distinct toxicity to particular organisms, speciation changes may significantly affect the final fate and bioeffects of AgNPs. However, as these two reverse processes occur simultaneously, it is difficult to monitor the reaction course, and rather large knowledge gaps exist, including the dominant process of the reactions, the reaction kinetics, and how environmental factors affect the transformation. To overcome these gaps, several methods have been developed based on labeled NPs and ions, including labeling with radioisotopes, enriched stable isotopes and dyes/phase contrasting agents.²⁷ Among these labeling methods, stable isotope tracing is much more preferred due to its easy handling and no need for required post-synthesis manipulation.^{27–29} The stable isotope labeling method has been used to detect the toxicity and bioaccumulation of several types of NPs with high sensitivity and reliability.^{27,28,30–34}

In this study, we synthesized isotopically labeled AgNPs (99.5% ¹⁰⁷Ag, ¹⁰⁷AgNPs) and AgNO₃ (99.81% ¹⁰⁹Ag, ¹⁰⁹AgNO₃).

For the first time, two stable Ag isotopes were used in the same experiment to track the transformation kinetics of AgNPs and Ag⁺ independently in aquatic environments. The effects of several key environmental factors such as sunlight, DOM, solution pH, temperature, and divalent cations on the reaction kinetics were evaluated thoroughly, which would deepen our insight into the environmental behavior of AgNPs.

2. Experimental

2.1. Materials

AgNO₃ (>99.5% purity) and ultrapure silver foil (>99.9% purity) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). ¹⁰⁷Ag and ¹⁰⁹Ag isotopes (99+% enriched) in solid form were purchased from Trace Sciences International Inc. (Pilot Point, TX). Trisodium citrate dihydrate (>99% purity), sodium borohydride (>99.99%, trace metals basis) and 2-(*N*-morpholino)ethanesulfonic acid (>99% purity) were purchased from Sigma Aldrich. High purity nitric acid was purchased from Merck (Darmstadt, Germany). Suwannee river humic acid (SRHA) was from the International Humic Substances Society (IHSS, St. Paul, MN). The Ag⁺ standard (1000 mg L⁻¹) used for ICP-MS determination was from National Institute of Metrology (Beijing, China). Other reagents were purchased from Beijing Chemicals and were of analytical purity or higher (Beijing, China). All the reagents were used as obtained without further purification. Ultrapure water (18.3 MΩ) produced with a Milli-Q Gradient system (Millipore, Billerica, MA) was used throughout the experiments.

2.2. Synthesis of the isotopically enriched AgNPs and Ag⁺

Citrate-coated AgNPs (with natural isotope abundances) were synthesized following a previously reported method with slight modifications.^{29,35} Briefly, 0.43 mL of 58.8 mmol L⁻¹ AgNO₃ and 3.7 mL of 34 mmol L⁻¹ trisodium citrate dihydrate were added into 100 mL of boiling distilled water, and then 1 mL of 50 mmol L⁻¹ sodium borohydride was added drop-wise into the solution with vigorous stirring. The solution turned from colorless to yellow immediately, and the color deepened with further addition of sodium borohydride. After stirring for another 30 min, the reaction vessel was removed from the heating plate and allowed to cool to room temperature. The soluble byproducts were removed by centrifugal ultrafiltration (Amicon Ultra-15 100 kD, Millipore, MA), and the AgNPs were further purified by washing with ultrapure water three times, after which the stock suspension was stored at 4 °C in the dark for later use. For the synthesis of ¹⁰⁷AgNPs, the only difference was that the ¹⁰⁷Ag isotope metal was first dissolved in HNO₃, followed by evaporation to dryness to afford the nitrate salt. ¹⁰⁹AgNO₃ was also obtained by dissolving the ¹⁰⁹Ag isotope metal in HNO₃. Silver foil with natural isotope abundances was used to optimize the synthesis parameters first.

2.3. Characterization of AgNPs

Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) analysis were carried out with an H-7500 (Hitachi, Japan) at 80 kV or high resolution TEM coupled with EDS (TECNAI G20, FEI, Hillsboro OR) at 200 kV. TEM samples were prepared by placing 5 μ L aliquots of the aqueous sample onto an ultrathin carbon-coated copper grid and drying in a vacuum drying oven. The UV-vis spectra from 250–800 nm were obtained using a Shimadzu UV-3600 (Kyoto, Japan). The ζ potential and hydrodynamic diameter of the AgNPs were characterized by dynamic light scattering (DLS) with a Zetasizer Nano (Malvern Instruments Ltd, Malvern, UK) at 25 °C. Specifically, stock AgNP suspensions were diluted with ultrapure water to a final concentration of 10 mg L⁻¹, and three measurements were performed to get the average value. The polydispersity index (PDI), reported directly from the Zetasizer Nano ZS instrument when measuring the average hydrodynamic diameter, was also recorded to interpret the broadness of the size distribution.

2.4. Natural organic matter solutions

SRHA was prepared at 1 g L⁻¹ in ultrapure water and dissolved overnight on an end-over-end rotator at room temperature and then filtered through 0.45 μ m membrane filters (mixed cellulose esters, Millipore, Billerica, MA). The dissolved organic carbon (DOC) was measured with a Phoenix 8000 total organic carbon analyzer (Tekmar-Dohrmann, Cincinnati, OH).

2.5. Silver transformation experiment

The experiments were conducted in a solar simulator (Beifanglihui CO., SN-500, Beijing) equipped with three 2500 W Xe lamps to simulate the sunlight. The irradiation intensity was maintained at 550 W m⁻², and the bottles were immersed in a recirculating cooling water system to control the temperature. Three hundred milliliter suspensions containing 1 mg L⁻¹ ¹⁰⁷AgNPs and 1 mg L⁻¹ ¹⁰⁹Ag⁺ were prepared in 500 mL FEP (fluorinated ethylene propylene) bottles (Nalgene, Rochester, NY). For general experiments, the pH was set to 7.4 and the temperature was 30 °C. For each batch of the experiment, a dark control was performed in FEP bottles wrapped in three layers of aluminum foil and then one layer of black plastic bags and placed in the same simulator under similar conditions to the light-exposed ones. The effects of different parameters on the transformation of silver were evaluated. SRHA with a final concentration of 5 mg C L⁻¹ was added to the system to investigate the effect of DOM. Silver transformation was also conducted in the presence of SRHA at different pH values (5.6, 7.4 and 8.5). MES (2-(*N*-morpholino)ethanesulfonic acid) buffer (10 mM, pH 5.6) and borate buffers (1 mM, pH 7.4 and 8.5) were used to control the pH, and diluted HNO₃ and NaOH were used to adjust the pH values. Moreover, the effect of temperature (6, 30 and 50 °C) and divalent cations (40 mg L⁻¹ Ca²⁺ and 24 mg L⁻¹ Mg²⁺) on the transformation kinetics of silver were also assessed. Stock solutions of Ca(NO₃)₂ and Mg(NO₃)₂ were pre-

pared at concentrations of 40 and 24 g L⁻¹ in ultrapure water. At each time interval during the experiment, 5 mL of the sample was taken from the bottle and mixed with 2.5 mL saturated EDTA solution for 10 min. Then the dissolved Ag was separated from the AgNPs using ultrafiltration. The detailed separation method is shown in the following section 2.6. The filtrate was collected for further analysis after separation. Meanwhile, another 3 mL of the sample was taken to measure the UV-vis spectra. Three independent bottles were conducted for each experiment.

2.6. Separation of AgNPs and Ag⁺

In our previous study, the ultrafiltration method proved to be an efficient approach for separating AgNPs and Ag⁺, and the adsorption of Ag⁺ on separation devices (Amicon Ultra-15 30 kD, Millipore, MA) was insignificant with a recovery higher than 80%.²⁶ The same concentration of ¹⁰⁷AgNPs was used in this study, so the ultrafiltration method was also employed. It was reported that Ag⁺ could easily adsorb onto AgNP surfaces, resulting in an obvious decrease in free Ag⁺.¹² The depletion of measured free Ag⁺ in our case may cause deviation of the AgNP transformation kinetics. Therefore, EDTA, which was demonstrated to be able to efficiently eliminate the co-extraction of Ag⁺ with AgNPs in previous studies,³⁶ was used as a complexing agent to reduce the adsorption of Ag⁺ on the surfaces of AgNPs in the experiment. To confirm that EDTA could not enhance the dissolution of AgNPs, suspensions containing 1 mg L⁻¹ AgNPs and 100 mM EDTA (concentrations used in the experiment) were prepared and kept in the dark. At time intervals of 5 min, 10 min and 20 min, 5 mL of each sample was taken out to determine the dissolved Ag⁺ concentration after ultrafiltration. No significant difference was observed. In our experiment, samples were mixed with EDTA for 10 min before ultrafiltration. Therefore, the effect of EDTA on the dissolution of the AgNPs was negligible. By using the centrifugal ultrafiltration tubes (30 kD), AgNPs as small as 2 nm could be retained in the upper filter devices.²⁶ We cannot exclude that some tiny AgNPs smaller than 2 nm may escape from the membrane, so in all cases in our study the dissolved Ag refers to all the dissolved Ag species that could pass through the filtration membranes, including mainly free Ag⁺, SRHA associated Ag⁺, the adsorbed Ag⁺ and any AgNPs < 2 nm.

2.7. Quantification and calculation of tracer concentration

The ¹⁰⁷Ag and ¹⁰⁹Ag concentrations of the stock solutions (¹⁰⁷AgNPs and ¹⁰⁹AgNO₃) and the filtrates after separation were determined using Agilent 7700 ICP-MS (Santa Clara, CA, limit of detection of 0.009 μ g L⁻¹), which was conducted with Ag standards, and the element In was used as the internal standard. For stock suspensions of ¹⁰⁷AgNPs, HNO₃ digestion was performed before analysis. Briefly, 100 μ L ¹⁰⁷AgNPs was mixed with 2 mL high purity HNO₃, and heated on a hot plate at 120 °C for 15 min. Then the solution was diluted for ICP-MS analysis. Blanks were conducted to account for potential contamination from reagents and containers, and the

silver contents in the blank samples were below the limit of detection of the ICP-MS. After the experiment, the silver loss due to adsorption on the inner walls of the bottles was also analyzed by decanting the solution and refilling the bottles with 1% HNO₃ followed by 4 h shaking to desorb the adsorbed silver.³⁷ Very limited silver (about 0.13% of the total silver content in the system) was detected by ICP-MS, showing that silver losses to the walls of the 500 mL FEP bottles were insignificant.

An isotope tracing technique was employed to track two tracers, ¹⁰⁷Ag and ¹⁰⁹Ag, as described by Croteau *et al.*³³ Since the concentration of silver in the reagents and container blanks was below the limit of detection of the ICP-MS, we assume that the silver present in the system was only from the two isotopes we added. Though the enrichment of the two isotopes was not 100% (99.5% for ¹⁰⁷Ag and 99.81% for ¹⁰⁹Ag), the effect of ultratrace impurities on the final data was very limited. Therefore, we also assume that 100% ¹⁰⁷Ag was from the ¹⁰⁷Ag enriched source and likewise for ¹⁰⁹Ag. The relative abundances of the ¹⁰⁷Ag tracer (p^{107}) and ¹⁰⁹Ag tracer (p^{109}) in the calibration standards were also determined using the signal intensities of each Ag isotope (eqn (1) and (2)).^{30,33} p^{107} averaged 0.5150 ± 0.0037 (standard deviation) and p^{109} averaged 0.4850 ± 0.0037 for batches of samples analyzed on different days, which were in agreement with the natural relative abundances of ¹⁰⁷Ag (0.5184) and ¹⁰⁹Ag (0.4816),²⁹ showing the obtained data were convincing.

$$p^{107} = \text{intensity} \left(\frac{{}^{107}\text{Ag}}{{}^{107}\text{Ag} + {}^{109}\text{Ag}} \right) \quad (1)$$

$$p^{109} = \text{intensity} \left(\frac{{}^{109}\text{Ag}}{{}^{107}\text{Ag} + {}^{109}\text{Ag}} \right) \quad (2)$$

The concentration of the tracer ¹⁰⁷Ag in the filtrate ($[{}^{107}\text{Ag}]$) was calculated as the product of p^{107} and the total Ag concentration given by the ICP-MS software from the tracer intensity ($[T^{107}\text{Ag}]$), and the concentration of the tracer ¹⁰⁹Ag in the filtrate ($[{}^{109}\text{Ag}]$) was calculated as the product of p^{109} and the total Ag concentration given by the ICP-MS software from the tracer intensity ($[T^{109}\text{Ag}]$):

$$[{}^{107}\text{Ag}] = p^{107}[T^{107}\text{Ag}] \quad (3)$$

$$[{}^{109}\text{Ag}] = p^{109}[T^{109}\text{Ag}] \quad (4)$$

3. Results and discussion

3.1. Characterization and stability of AgNPs

As shown in Fig. S1,† the synthesized citrate-coated ¹⁰⁷AgNPs in this study are almost spherical with a mean size of 15.6 ± 4.3 nm, calculated by manually counting more than 200 individual particles. ¹⁰⁷AgNPs carried stable negative charges with

a ζ potential of -23.1 mV in ultrapure water, and *in situ* DLS gave a hydrodynamic diameter of 24.7 nm, larger than the TEM result due to the citrate coating, with a PDI of 0.378. Compared with previous reports²⁹ using the same method for the synthesis of ¹⁰⁷Ag labeled NPs, we can get a comparable particle size, shape and size distribution, proving this method is quite reproducible. Though the enriched stable isotopes are expensive, this synthesis method provides a high yield (an average yield of 78%) and only requires several mg for a single synthesis,²⁹ which is affordable. During storage, a portion of the stock suspension was taken out for DLS analysis every month and the results showed that no significant difference of the hydrodynamic diameter and ζ potential was observed over three months, revealing the ¹⁰⁷AgNP suspension was rather stable. In the experiment, the stock suspension was kept for no more than three months.

3.2. Effect of light irradiation

Diluted ¹⁰⁷AgNPs (1 mg L^{-1}) and ¹⁰⁹Ag⁺ (1 mg L^{-1}) solutions were mixed together, and subjected to solar irradiation or kept in the dark to evaluate the effect of simulated sunlight on the transformation of AgNPs and Ag⁺. As AgNPs are highly dynamic, oxidation of AgNPs to release Ag⁺ is expected to take place in the suspension.^{12,26} Moreover, the reduction of Ag⁺ to Ag⁰ by some capping agents was also reported in early studies.³⁸ Therefore, we first monitored the time-resolved concentration of dissolved ¹⁰⁷Ag⁺ and ¹⁰⁹Ag⁺ during the experiment. As shown in Fig. 1A, the amount of dissolved ¹⁰⁹Ag⁺ only fluctuated on a very small scale both in the light and dark, and did not change much over the whole time, indicating that the reduction of Ag⁺ in simple AgNP suspensions was not evident without additional reducing agents even under solar irradiation. On the contrary, the concentration of dissolved ¹⁰⁷Ag⁺ increased rapidly in both cases, implying the fast oxidation of ¹⁰⁷AgNPs. It is noteworthy that the initial concentration of ¹⁰⁷Ag⁺ was not zero, and about $100 \mu\text{g L}^{-1}$ ¹⁰⁷Ag⁺ was detected in the system. The inevitable exposure to oxygen during dilution of the stock suspensions may lead to the oxidation of AgNPs.¹⁶ Furthermore, as the complexing agent EDTA was added during the separation procedure, the high concentration of ¹⁰⁷Ag⁺ may also be ascribed to adsorbed ¹⁰⁷Ag⁺ on the surfaces of ¹⁰⁷AgNPs, because $50.6 \mu\text{g L}^{-1}$ ¹⁰⁷Ag⁺ was measured without EDTA. A previous study also reported that the addition of 2 mg L^{-1} AgNPs into 0.3 mg L^{-1} Ag⁺ solution led to a rapid decrease (about $100 \mu\text{g L}^{-1}$) in the dissolved Ag⁺ concentration.

According to previous studies, the oxidation reaction of AgNPs can be written as given in eqn (5):¹²

The concentrations of H⁺ and dissolved O₂ are supposed to be constant over time, so the oxidation of ¹⁰⁷AgNPs followed a pseudo first-order rate law:¹⁶

Fig. 1 Transformation of AgNPs and Ag^+ in pure water. Change of dissolved $^{109}\text{Ag}^+$ over time (A); fraction of metallic $^{107}\text{AgNPs}$ over time (B); and TEM images of AgNPs in the dark after 0 h (C) and 48 h (D), and in the light after 8 h (E) and 48 h (F). A mixture of $1 \text{ mg L}^{-1} ^{107}\text{AgNPs}$ and $1 \text{ mg L}^{-1} ^{109}\text{Ag}^+$ in pure water was treated at pH 7.4 and 30°C .

$$[^{107}\text{Ag}^+]_t = [^{107}\text{Ag}^+]_0 [1 - \exp(-kt)] \quad (6)$$

in which $[^{107}\text{Ag}^+]_t$ is the released concentration of $^{107}\text{Ag}^+$ at time t , $[^{107}\text{Ag}^+]_0$ is the concentration of $^{107}\text{AgNPs}$ at the beginning of the experiment, k is the rate constant, and t is the reaction time. Taking the logarithm of eqn (6), we get the following equation:

$$\ln \left(\frac{[^{107}\text{Ag}^+]_0 - [^{107}\text{Ag}^+]_t}{[^{107}\text{Ag}^+]_0} \right) = -kt \quad (7)$$

We assume that 100% ^{107}Ag was from a ^{107}Ag enriched source, so $[^{107}\text{Ag}^+]_t$, the concentration of $^{107}\text{AgNPs}$ at time t ,

can be obtained from the difference of the concentration of $^{107}\text{AgNPs}$ at initial time ($[^{107}\text{Ag}^+]_0$) and the released concentration of $^{107}\text{Ag}^+$ at time t ($[^{107}\text{Ag}^+]_t$). Thus, eqn (7) can be written as:

$$\ln \left(\frac{[^{107}\text{Ag}^+]_0 - [^{107}\text{Ag}^+]_t}{[^{107}\text{Ag}^+]_0} \right) = -kt \quad (8)$$

The curve obtained by plotting $\ln \left(\frac{[^{107}\text{Ag}^+]_0 - [^{107}\text{Ag}^+]_t}{[^{107}\text{Ag}^+]_0} \right)$ versus time for $^{107}\text{AgNPs}$ (Fig. 1B) in the dark is linear with $R^2 = 0.9787$, indicating that the ion release of $^{107}\text{Ag}^+$ obeyed first-order

kinetics well. However, the fitting line was divided into two stages for the experiment in the light. During the first 12 h, the oxidation of $^{107}\text{AgNPs}$ was much more rapid with a dissolution rate constant of 0.0366 h^{-1} , about 4 times higher than that for the experiment in the dark. Light induced fast dissolution of AgNPs was also observed in other studies,²⁶ and photo-aging, which causes a gradual formation of an oxide shell around metallic silver cores under light irradiation, may shed some light on the phenomenon.³⁹ After 12 h, the release rate of $^{107}\text{Ag}^+$ slowed down. Considering that solar irradiation could degrade the capping agents of AgNPs, such as citrate and PVP, which may induce the aggregation of AgNPs,^{26,37,40–42} we speculate that the decreased oxidation rate was ascribed to the coarsening of $^{107}\text{AgNPs}$. A previous study also reported that a loss of accessibility of reactive sites, due to the aggregation process, decreased the dissolution rate constant of the AgNPs.⁴³ To this end, the UV-vis spectra of AgNPs at different time intervals were measured (Fig. S2†). The SPR peak position for the experiment in the dark did not alter dramatically except for a decrease in the absorption with time and a small blue shift of λ_{max} , implying that the $^{107}\text{AgNPs}$ were rather stable in the dark without agglomeration. For $^{107}\text{AgNPs}$ under solar irradiation, no significant change in the SPR peak shape was observed during the first 8 h; however, obvious broadening of the peak width occurred after that, indicating aggregation of the $^{107}\text{AgNPs}$. Meanwhile, we monitored the morphology change of the AgNPs by TEM. Fig. 1C and D show that the $^{107}\text{AgNPs}$ in the dark were well-dispersed even after 2 days' reaction. However, a light-triggered shape transformation was observed for $^{107}\text{AgNPs}$ exposed to simulated sunlight. In accord with the UV-vis spectra results, $^{107}\text{AgNPs}$ were stable in the first several hours (Fig. S2C†). However, with longer solar irradiation, adjacent particles tended to fuse together to form larger particles and worm-like structures (Fig. 1E), which explains the SPR peak broadening in the UV-vis spectra. As time went on, more particles were involved to form large aggregates (Fig. 1F), causing a significant decrease of the $^{107}\text{AgNPs}$ ' surface areas, which may contribute to the retarded release rate of $^{107}\text{Ag}^+$ in the light.

3.3. Effect of dissolved organic matter

Our earlier study reported that the oxidation of AgNPs to release Ag^+ and the reduction of Ag^+ to form new AgNPs by DOM could both happen in sunlit DOM-rich water, which considerably affected the fate and transport of AgNPs in the environment.²⁶ In order to gain important information on these two reverse processes, SRHA, used as a model HA, was added to the mixture of $^{107}\text{AgNPs}$ and $^{109}\text{Ag}^+$ to evaluate the reaction kinetics. The real-time contents of dissolved Ag^+ in the light and dark were both recorded. The concentration of dissolved $^{109}\text{Ag}^+$ decreased dramatically in both cases, revealing the fast reduction of Ag^+ by SRHA. According to previous studies, the reduction of Ag^+ by DOM obeyed pseudo-first-order reaction kinetics;²³ that is:

$$\frac{d[^{109}\text{AgNP}]}{dt} = k[^{109}\text{Ag}^+]_t \quad (9)$$

where $d[^{109}\text{AgNP}]$ is the concentration change of $^{109}\text{AgNPs}$ in a short period of time dt , $[^{109}\text{Ag}^+]_t$ is the concentration of $^{109}\text{Ag}^+$ at time t , and k is the rate constant.

Here we assume that all the reduced $^{109}\text{Ag}^+$ was transformed into $^{109}\text{AgNPs}$ in the presence of SRHA, so $[^{109}\text{AgNP}]$ can be obtained by the difference of the concentration of $^{109}\text{Ag}^+$ at the initial time ($[^{109}\text{Ag}^+]_0$) and at time t ($[^{109}\text{Ag}^+]_t$). After integration, eqn (9) can be written as:

$$[^{109}\text{Ag}^+]_t = [^{109}\text{Ag}^+]_0 \exp(-kt) \quad (10)$$

Taking the logarithm of eqn (10), we get the following equation:

$$\ln\left(\frac{[^{109}\text{Ag}^+]_t}{[^{109}\text{Ag}^+]_0}\right) = -kt \quad (11)$$

Eqn (11) fit well to the data of dissolved $^{109}\text{Ag}^+$ (Fig. 2A), and the reduction rate constant under solar irradiation (0.0051 h^{-1}) was approximately 2 times larger than that in the dark (0.0017 h^{-1}), revealing that sunlight greatly promoted the regeneration of AgNPs.^{22,23} Additionally, we also took TEM images to confirm the formation of new AgNPs. As shown in Fig. 2C and S3†, a large number of small NPs in the size range of 2–6 nm appeared around the original AgNPs (about 15 nm) both in the light and dark after 24 h. High resolution TEM images (Fig. 2D and S3B†) demonstrated that the lattice fringe spacing of these small NPs was about 2.4 Å, corresponding to the (111) lattice plane of the face-centered cubic structure of metallic silver. Moreover, the EDS data (Fig. 2E and S3C†) also shows high signals for Ag, proving the small particles were AgNPs. The strong signals of Cu and C were mostly attributed to the carbon supported copper grid. As the original $^{107}\text{AgNPs}$ had a narrow size distribution, and the release of $^{107}\text{Ag}^+$ was not high (Fig. 2B, only about 17% silver was in ionic form), we can exclude the possibility that the dissolution of pristine $^{107}\text{AgNPs}$ (15 nm) gave rise to the formation of small AgNPs (2–6 nm).

Since the recrystallization of AgNPs from Ag^+ could not be ignored, the measured data of dissolved $^{107}\text{Ag}^+$ was corrected based on the fitted reduction equation given in Fig. 2A, and the corrected ion release kinetics of $^{107}\text{AgNPs}$ is shown in Fig. 2B. The concentration of dissolved $^{107}\text{Ag}^+$ gradually increased due to oxidation of the $^{107}\text{AgNPs}$. However, after about 12 h, the curve dropped sharply for experiments both in the light and dark. The maximum concentration of dissolved $^{107}\text{Ag}^+$ was much lower than that without SRHA as well. The inhibited ion release of AgNPs in the presence of DOM has been extensively reported elsewhere, and was ascribed to either blocking of the oxidation sites of AgNPs due to the adsorption of DOM, or the reduced amount of peroxide intermediates owing to their competitive reaction with DOM.^{12,26} As the amount of dissolved $^{107}\text{Ag}^+$ reconstituted to

Fig. 2 Transformation of AgNPs and Ag^+ in the presence of SRHA. Fraction of dissolved $^{109}\text{Ag}^+$ over time (A); ion release kinetics of $^{107}\text{AgNPs}$ over time (B); and TEM image of AgNPs in the light after 24 h (C), and the high resolution TEM image (D) and EDS analysis (E) of the new AgNPs. A mixture of 1 mg L^{-1} $^{107}\text{AgNPs}$, 1 mg L^{-1} $^{109}\text{Ag}^+$ and 5 mg C L^{-1} SRHA was treated at pH 7.4 and 30°C .

$^{107}\text{AgNPs}$ had been compensated for by the fitted reduction equation, the unusual decrease of dissolved $^{107}\text{Ag}^+$ indicates that there might be other pathways that contribute to the $^{107}\text{Ag}^+$ reduction. For example, previous studies have shown that AgNPs could serve as catalysts to facilitate the reduction of Ag^+ on their surfaces, which resulted in a rapid AgNP growth stage.^{20,44–47} In our study, the initial concentration of $^{109}\text{Ag}^+$ in the solution was relatively high, and the coating of SRHA on AgNPs also provided a physical barrier that made it harder for the released $^{107}\text{Ag}^+$ to diffuse into the bulk solution. As a result, most of $^{107}\text{Ag}^+$ might adsorb on the surfaces of the $^{107}\text{AgNPs}$ or stay around the $^{107}\text{AgNP}$ cores, which promoted the autocatalysis by the $^{107}\text{AgNPs}$. However, as the oxidation of $^{107}\text{AgNPs}$ happened at the same time, it was impossible to trace the autocatalysis process. Compared with the rapid reduction of $^{109}\text{Ag}^+$, the oxidation of $^{107}\text{AgNPs}$ is very limited. Therefore, the dissolution of formed $^{109}\text{AgNPs}$ should be unremarkable in our study.

3.4. Effect of pH

pH is an important parameter that may influence the thermodynamic equilibrium of AgNPs,¹² thus the reaction kinetics of $^{107}\text{AgNPs}$ and $^{109}\text{Ag}^+$ at different pH values was evaluated in this study. In the tested pH range (5.6–8.5), there is an obvious decrease in the concentration of $^{109}\text{Ag}^+$ during the experiment. By fitting the collected data to eqn (11), linear

lines were obtained. The reaction rate coefficient increased (the slope of the lines became more negative) with the increasing solution pH. As shown in Fig. 3, the reaction rate constant under solar irradiation increased about 4 times from 0.0025 h^{-1} at pH 5.6 to 0.0098 h^{-1} at pH 8.5, which also happened for the equivalent dark reaction, though the reaction rate coefficient was much lower. pH-dependent reduction of Ag^+ was also reported in prior studies.^{22,23} It was demonstrated that there existed a linear relationship between the redox potential of the HA solution and the pH, and the much lower redox potential of HA at higher pH accelerated the reduction of Ag^+ .²² The ligand-to-metal charge transfer pathway was also reported to be involved in the reduction of Ag^+ , in which Ag^+ first bound to HA and electron transfer between Ag^+ and HA induced the AgNP generation. At high pH, HA was more negative and a strong electrostatic attraction between the positively charged Ag^+ and negatively charged HA enhanced the complexation of HA with Ag^+ , thus promoting the Ag^+ reduction.²³

The concentration of dissolved $^{107}\text{Ag}^+$ showed a similar trend at pH 5.6 to that at pH 7.4 after correction, which first increased for some time and then decreased gradually, suggesting that an autocatalysis process may occur as well. As oxygen and protons both participated in the oxidation of AgNPs,¹² the lower pH facilitated the dissolution of the AgNPs, which explained the higher concentration of dissolved $^{107}\text{Ag}^+$ at pH 5.6. However, the dissolution behavior

Fig. 3 Fraction of dissolved $^{109}\text{Ag}^+$ and ion release kinetics of $^{107}\text{AgNPs}$ over time at different pH values. Fraction of dissolved $^{109}\text{Ag}^+$ at pH 5.6 and 8.5 (A), ion release kinetics of $^{107}\text{AgNPs}$ at pH 5.6 (B), fraction of dissolved $^{107}\text{Ag}^+$ at pH 8.5 (C). A mixture of 1 mg L^{-1} $^{107}\text{AgNPs}$, 1 mg L^{-1} $^{109}\text{Ag}^+$, and 5 mg C L^{-1} SRHA was treated at 30°C .

of AgNPs at pH 8.5 was different. The measured $^{107}\text{Ag}^+$ concentration dropped from that at the beginning of the reaction. As $^{107}\text{Ag}^+$ could also be reduced by DOM, we can get a similar equation to eqn (11):

$$\ln\left(\frac{[^{107}\text{Ag}^+]_t}{[^{107}\text{Ag}^+]_0}\right) = -kt \quad (12)$$

The measured $^{107}\text{Ag}^+$ concentration fitted well with eqn (12). Furthermore, the reaction rate coefficients were almost equal to those of the reduction of dissolved $^{109}\text{Ag}^+$ under the same conditions (0.0051 h^{-1} for $^{109}\text{Ag}^+$ vs. 0.0052 h^{-1} for $^{107}\text{Ag}^+$ in the dark and 0.0098 h^{-1} for $^{109}\text{Ag}^+$ vs. 0.010 h^{-1} for $^{107}\text{Ag}^+$ in the light), which indicated that the oxidation of the $^{107}\text{AgNPs}$ was negligible. Compared with our previous study,²⁶ though the dissolution of AgNPs was not favored at high pH, the release of Ag^+ was still detectable in AgNP suspensions at pH 8.3 under similar conditions. The varied behavior of the AgNPs implied that the pre-addition of Ag^+ in the system affected the Ag^0/Ag^+ coexistence equilibrium of the AgNPs, which may subsequently influence the final fate and transformation of the AgNPs.

3.5. Effect of temperature

The influence of temperature on the reaction kinetics was also evaluated. Results (Fig. S4A†) showed that an increase of temperature accelerated the reduction of $^{109}\text{Ag}^+$, resulting in larger reaction rate constants both in the light and dark. However, a higher temperature had little influence on the dissolution of $^{107}\text{Ag}^+$ (Fig. S4B†), probably because the presence of large amounts of dissolved $^{109}\text{Ag}^+$ in the solution inhibited further oxidation of $^{107}\text{AgNPs}$. At low temperature, the reduction of $^{109}\text{Ag}^+$ was significantly retarded both in the light and dark, and the concentration of dissolved $^{109}\text{Ag}^+$ almost remained constant during the whole time (Fig. S4C†), which was also the case for the oxidation of $^{107}\text{AgNPs}$ in the dark. However, the concentration of dissolved $^{107}\text{Ag}^+$ progres-

sively increased under solar exposure even at 6°C (Fig. S4D†). Heat generation by metal NPs under optical illumination has been extensively studied^{48–50} and previous researchers have reported that the surface temperature of metal NPs could reach well above the boiling point of water under appropriate illumination.⁵⁰ The oxidation of $^{107}\text{AgNPs}$ at low temperature was mostly due to the photothermal effect of AgNPs, which emphasized that solar irradiation is a vital factor that cannot be ignored in assessing the environmental behavior of AgNPs.

3.6. Effect of Ca^{2+} and Mg^{2+}

Divalent metal ions like Ca^{2+} and Mg^{2+} are ubiquitous in natural water, and they can largely affect the stability and transport of NPs.^{37,51} $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ were added at environmentally relevant concentrations to the system to assess their influence on the reaction kinetics. The solution turned from yellow to dark red upon spiking of $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$. Meanwhile, time-dependent UV-vis spectra (Fig. 4) also showed a tailing peak following the main SPR peak, suggesting that divalent metal ions triggered the aggregation of AgNPs. For samples kept in the dark, the characteristic SPR absorption did not change much over time, while the absorption of the tail peak gradually grew with longer light irradiation, indicating further agglomeration of the AgNPs, which again proved the significant effect of light on the transformation of AgNPs. The related shape transformation of AgNPs was confirmed by the following TEM images. From Fig. 4E, the bridging of neighboring AgNPs after the addition of divalent metal ions is clearly observed. Compared with the presence of small coagulations in the dark after the experiment, particles exposed to light appeared to be relatively more agglomerated. A larger number of initial AgNPs and regenerated tiny particles participated in the growing of large aggregates, resulting in amorphous structures.

Though AgNPs aggregated in the presence of divalent metal ions, the reduction of $^{109}\text{Ag}^+$ was not strongly affected, as the variation of the fitted reaction rate coefficients was

Fig. 4 Impact of divalent cations on the transformation of AgNPs and Ag⁺. UV-vis absorption spectra of AgNPs: in the light (A) and dark (B); fraction of dissolved ¹⁰⁹Ag⁺ (C) and ion release kinetics of ¹⁰⁷AgNPs (D) over time; and TEM images of AgNPs in the presence of divalent cations after 0 h (E), 48 h in the dark (F) and 48 h under solar irradiation (G); the scale bar is 100 nm. A mixture of 1 mg L⁻¹ ¹⁰⁷AgNPs, 1 mg L⁻¹ ¹⁰⁹Ag⁺, 5 mg C L⁻¹ SRHA, 40 mg L⁻¹ Ca²⁺, and 24 mg L⁻¹ Mg²⁺ was treated at pH 7.4 and 30 °C.

very limited (0.0017 h⁻¹ with divalent ions vs. 0.0017 h⁻¹ without divalent ions in the dark, and 0.0048 h⁻¹ with divalent ions vs. 0.0051 h⁻¹ without divalent ions in the light). This was likely due to the reduction of ¹⁰⁹Ag⁺ taking place in homogeneous solutions which were not greatly influenced by the shape shift of ¹⁰⁷AgNPs. As for the release of ¹⁰⁷Ag⁺, since the aggregation of ¹⁰⁷AgNPs considerably reduced the effective surface areas, the oxidation of ¹⁰⁷AgNPs was hindered in the dark, resulting in a negligible change of the concentration of dissolved ¹⁰⁷Ag⁺. However, because of the photo-thermal effect of light, an evident increase of dissolved ¹⁰⁷Ag⁺ was still measured. The decrease of the surface areas of ¹⁰⁷AgNPs may restrict the autocatalysis reaction on the surface of ¹⁰⁷AgNPs; thus, the subsequent decrease of dissolved ¹⁰⁷Ag⁺ became much slower.

To compare the influence of individual environmental factors on the transformation kinetics of AgNPs and Ag⁺ in aquatic systems, all the reaction kinetic constants are summarized in Tables S1 and S2 of the ESI.†

4. Conclusions

Our previous study²⁶ has shown that inevitable environmentally relevant factors such as sunlight and DOM can influence the transformation of AgNPs in aquatic systems. The cycle of chemical oxidation of AgNPs to release Ag⁺ and regeneration to form AgNPs exists in sunlit DOM-rich water. However, as the two reverse processes occur simultaneously, it is difficult to monitor the reaction course, which leaves large knowledge gaps, such as the dominant process of the reactions, the

reaction kinetics, and how environmental factors affect the transformation kinetics. In this work, a double stable isotope labeling method (stable isotope labeled $^{107}\text{AgNPs}$ and $^{109}\text{AgNO}_3$ mixed in the same experiment) was used to investigate the speciation variation of silver in the water column, and much more information on the transformation kinetics of silver was obtained. In pure water containing both $^{107}\text{AgNPs}$ and $^{109}\text{Ag}^+$, the oxidation of $^{107}\text{AgNPs}$ dominated the reaction, resulting in a substantial content of total dissolved Ag^+ . Sunlight played dual functions in the process. On the one hand, solar exposure greatly accelerated the oxidation of $^{107}\text{AgNPs}$, and a much higher initial reaction rate constant was obtained than for the reaction in the dark (0.0366 h^{-1} vs. 0.0078 h^{-1}). On the other hand, light irradiation induced the aggregation of $^{107}\text{AgNPs}$, causing the release of dissolved $^{107}\text{Ag}^+$ to slow down with time. However, the reduction of $^{109}\text{Ag}^+$ played the leading role in the presence of DOM, especially for samples under solar irradiation. The reaction rate coefficient was almost two times larger than the counterparts in the dark. DOM suppressed the oxidation of $^{107}\text{AgNPs}$, and only a small portion of dissolved $^{107}\text{Ag}^+$ was detected. Additionally, other reduction mechanisms might happen on the surface of $^{107}\text{AgNPs}$, causing the concentration of dissolved $^{107}\text{Ag}^+$ to decrease after some time. As Ag^+ has been shown to be much more toxic than AgNPs ,^{10,11,52} the reduction of dissolved Ag^+ in DOM-rich water suggests that the overall toxicity might be mitigated to some extent. Meanwhile, the enhanced stabilizing effect of DOM could disperse AgNPs in aquatic systems over a long time, which means that AgNPs may act as a reservoir of Ag^+ to cause persistent adverse effects. Furthermore, in areas where the use of AgNPs is not wide, there could still be some level of AgNPs due to the possible transport of AgNPs from the point of origin. At relatively low temperatures, though other reactions seemed to lag, the concentration of dissolved $^{107}\text{Ag}^+$ still increased gradually under solar irradiation, indicating the photothermal effects cannot be neglected. The spiking of divalent cations triggered agglomeration of $^{107}\text{AgNPs}$, but the reformation rate of $^{109}\text{AgNPs}$ was not greatly affected. According to previous studies,²² newly formed AgNPs were also prone to form large aggregates or even settle in the presence of Ca^{2+} and Mg^{2+} . The decrease in dissolved Ag^+ and coarsening of AgNPs may also alleviate AgNPs ' threat to aquatic organisms to a certain degree. It is reported that the estimated concentration of AgNPs in the river was in the range of $30\text{--}320\text{ ng L}^{-1}$ in the maximum scenarios,⁵³ which is much lower than that we used in our experiment. To better understand the fate of AgNPs in natural environments, further research exploring the transformation of AgNPs under more realistic conditions is needed.

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