



## Catalytic role of iron in the formation of silver nanoparticles in photo-irradiated $\text{Ag}^+$ -dissolved organic matter solution<sup>☆</sup>



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### ABSTRACT

Photo-reduction of  $\text{Ag}^+$  to silver nanoparticle (AgNPs) by dissolved organic matter (DOM) is a possible source of naturally occurring AgNPs. However, how this photo-reduction process is influenced by ubiquitous metal ions is still not well understood. In addition, in previous studies, the formation of AgNPs in DOM solution was usually monitored by UV-Vis spectroscopy, and there is still lack of quantitative analysis for the formed AgNPs. In the present study, the role of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  at environmental concentration level on this photochemical process was investigated, and the enhanced formation of AgNPs by  $\text{Fe}^{2+}/\text{Fe}^{3+}$  was probed and quantified by using UV-Vis spectroscopy, transmission electron microscopy, and liquid chromatography-inductively coupled plasma mass spectrometry. It was demonstrated that while  $\text{Fe}^{3+}$  can oxidize AgNPs to release  $\text{Ag}^+$ ,  $\text{Fe}^{2+}$  can reduce  $\text{Ag}^+$  into AgNPs. However, the DOM-induced reduction of  $\text{Fe}^{3+}$  makes iron an effective electron shuttle between DOM and  $\text{Ag}^+$ , and both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  enhanced AgNP formation. The impacts of environmentally relevant factors, including DOM concentration and solution pH, on this process were studied comprehensively, which showed that the catalytic role of iron was more significant at higher DOM concentration and lower pH. This iron-enhanced formation of AgNPs in photo-irradiated  $\text{Ag}^+$ -DOM solution have great environmental implications on the formation of natural AgNPs and the transformation of engineered AgNPs in acidic surface water with high iron content.

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## 1. Introduction

The antimicrobial capability of silver nanoparticles (AgNPs) and other conventional forms of silver (e.g., silver metal and silver salt) has been utilized in numerous consumer products and medical devices in recent years (Chernousova and Epple, 2013). In their production, use and disposal, the release of silver ion ( $\text{Ag}^+$ ) and AgNPs from these silver-containing consumer products and medical devices is inevitable (Benn and Westerhoff, 2008; Geranio et al., 2009; Gottschalk and Nowack, 2011; Mitrano et al., 2014). The released AgNPs readily transform in the environment through processes like oxidative dissolution (Dobias and Bernier-Latmani, 2013; Liu and Hurt, 2010; Liu et al., 2010) and sulfidation (Levard

et al., 2011; Liu et al., 2011), which not only modifies their properties, but also have great impacts on their transport, bioavailability, and toxicity (Levard et al., 2012). The oxidative dissolution of AgNPs releases  $\text{Ag}^+$ , which increases the toxicity of AgNP significantly (Kittler et al., 2010; Xiu et al., 2012; Yang et al., 2012). However, recently it was also discovered that ubiquitous dissolved organic matter (DOM) can reduce  $\text{Ag}^+$  into AgNPs with DOM as both reductant and coating agent (Adegboyega et al., 2013; Akaighe et al., 2011; Hou et al., 2013; Yin et al., 2012, 2014). This reduction process is not only a possible source of naturally occurring AgNPs (Akaighe et al., 2011; Yin et al., 2012), but also has great impacts on the fate and transformation of engineered AgNPs (Yu et al., 2014). Further studies showed that this reduction process is influenced by thermal (Adegboyega et al., 2013; Akaighe et al., 2011) or sunlight irradiation (Hou et al., 2013; Yin et al., 2012), pH (Hou et al., 2013; Yin et al., 2012), source (Akaighe et al., 2011; Yin et al., 2012) and redox states of DOM (Maurer et al., 2012). However, effect of ubiquitous metal ions on this reduction process is still largely

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unknown. In aquatic ecosystems, light-induced redox cycling of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  plays important role in numerous chemical processes (Emmenegger et al., 2001; Song et al., 2005), e.g., the catalytic reduction of Cr(VI) (Agrawal et al., 2009; Gaberell et al., 2003). Recently, Adegboyega et al. showed that  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$  ions in the mixtures of  $\text{Ag}^+$  and DOM enhanced the formation of AgNPs under heating (90 °C) (Adegboyega et al., 2014) or UV irradiation (Adegboyega et al., 2016). However, how the presence of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in  $\text{Ag}^+$ -DOM system on the formation of AgNPs under other more environment-relevant conditions (e.g., under sunlight irradiation) is still not well understood. In addition, in previous studies, the formation of AgNPs in DOM solution was usually monitored by UV-Vis spectroscopy (Adegboyega et al., 2014, 2016; Yin et al., 2012), and there is still lack of quantitative characterization for the formed AgNPs.

In the present study, we have demonstrated that the catalytic role of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  at environmental concentration level on the photo-reduction of  $\text{Ag}^+$  by DOM. The formation of AgNPs was demonstrated by using UV-Vis spectroscopy and transmission electron microscopy (TEM), and further quantitative analysis for the formed AgNPs was performed by using the liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP-MS). Environmental factors including the DOM concentration and solution pH, have been studied comprehensively, focusing on the catalytic role of  $\text{Fe}^{2+}/\text{Fe}^{3+}$ . This  $\text{Fe}^{2+}/\text{Fe}^{3+}$ -enhanced formation of AgNPs in photo-irradiated  $\text{Ag}^+$ -DOM solution have great environmental implications on the formation of natural AgNPs and the transformation of engineered AgNPs in acidic surface water with high iron content.

## 2. Experimental section

### 2.1. Materials

$\text{AgClO}_4$ ,  $\text{Na}_2\text{B}_4\text{O}_7$ , and  $\text{H}_3\text{BO}_3$  were purchased from Beijing Chemicals (Beijing, China).  $\text{Fe}(\text{ClO}_4)_3$  (>98%) and  $\text{Fe}(\text{ClO}_4)_2$  (>98%) were from Sigma-Aldrich.  $\text{HNO}_3$  (65%) was from Merck (Darmstadt, Germany). Polyvinylpyrrolidone (PVP, molecular weight 58 000) was from Aladdin Chemistry Co. Ltd. (Shanghai, China). Water suspension of PVP-coated AgNPs (Lot number 10122203701) from Shanghai Huzheng Nanotechnology CO., Ltd. (Shanghai, China) was used to probe the oxidation of AgNPs by  $\text{Fe}^{3+}$ . The size distribution of these commercial AgNPs ( $24.3 \pm 10.1$  nm) was estimated by TEM using Nano Measurer 1.2 software and Gaussian fitting (Fig. S1). At least 300 particles were counted for the size distribution. Suwannee River Natural Organic Matter (Lot No. 1R101N) from the International Humic Substance Society (St. Paul, MN) was used as a DOM model. The dissolved organic carbon of the DOM solution was determined with a Phoenix 8000 UV-persulfate total organic carbon analyzer (Tekmar-Dohrmann, Cincinnati, OH). Other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) with grades of analytical or better. All the reagents were used as obtained without further purification. Ultrapure water (18.3 M $\Omega$ ) produced with a Milli Q Gradient system (Millipore, Billerica, MA) was used throughout the experiments.

### 2.2. Transformation of silver under dark or simulated sunlight

The experiments were performed in 100 mL quartz glass bottles with quartz caps under dark conditions or in a sunlight simulator (TEMI880, Beifang Lihui, Beijing, China) equipped with three wind-refrigerated 2500 W Xe lamp. The total volume of the solution was 100 mL. The intensity of the light was set as 550 W m $^{-2}$ . The spectrum of the simulated sunlight was given in our previous study (Yin et al., 2014). During the experiment, the reaction temperature

was maintained at ~35 °C by a water bath. Although phosphate is usually used as buffer to cover a wide range of pH, considering the low solubility of  $\text{Ag}_3\text{PO}_4$  in water ( $K_{\text{sp}}(\text{Ag}_3\text{PO}_4) = 1.46 \times 10^{-16}$ ) (Fu et al., 2007), phosphate is not a suitable buffer in our study. Therefore, acetic acid-acetate (pH 3.6), 2-(N-morpholino) ethanesulfonic acid (MES)-NaOH (pH 5.5 and 6.3), and borate (pH 7.4 and 8.0) were used as buffers for different pH conditions. The oxidation of AgNPs by  $\text{Fe}^{3+}$  and reduction of  $\text{Ag}^+$  by  $\text{Fe}^{2+}$  in the absence of DOM were performed at room temperature under dark or simulated irradiation. In the photo-irradiated  $\text{Ag}^+$ - $\text{Fe}^{2+}/\text{Fe}^{3+}$ -DOM systems, the parameters, including concentration of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and DOM, and pH of solution, were investigated, focusing on the catalytic role of  $\text{Fe}^{2+}/\text{Fe}^{3+}$ .

### 2.3. Characterizations and quantification of the species of silver

#### 2.3.1. UV-vis spectrometry

UV-vis spectra were recorded on a Shimadzu UV-vis-NIR Spectrophotometer (UV-3600, Japan). The wavelength scanning was performed from 200 to 800 nm at 0.5 nm wavelength interval.

#### 2.3.2. Transmission electron microscopy

TEM analysis was performed on a Hitachi H-7500 (Hitachi, Japan) or JEOL 2011 (Herts, England) transmission electron microscope. TEM samples were prepared by placing 5  $\mu\text{L}$  aliquots of the aqueous sample onto an ultrathin carbon-coated copper grid and drying at room temperature.

#### 2.3.3. Quantification of $\text{Ag}^+$ and AgNPs

The  $\text{Ag}^+$  in irradiated sample was quantified by LC-ICP-MS according to our previous study (Zhou et al., 2014). An amino column with the 500 Å pore size (Venusil Durashell-NH $_2$ , 5  $\mu\text{m}$  particle size, 250  $\times$  4.6 mm) purchased from Bonna-Agela Technologies Inc. (Tianjin, China) was used for the separation of  $\text{Ag}^+$  and AgNPs. The mobile phase was 0.1% (v/v) FL-70 (mixture of nonionic and anionic surfactants from Fisher Scientific, Fair Lawn, NJ) and 2 mmol L $^{-1}$   $\text{Na}_2\text{S}_2\text{O}_3$ . The column temperature and flow rate of mobile phase were set as 20 °C and 0.7 mL min $^{-1}$ , respectively. The injection volume was 100  $\mu\text{L}$ . Into 1 mL sample was added 20  $\mu\text{L}$  1 mol L $^{-1}$   $\text{Na}_2\text{S}_2\text{O}_3$ , and then the sample was injected for LC-ICP-MS measurement. Due to the complexation of  $\text{Ag}^+$  with  $\text{S}_2\text{O}_3^{2-}$  in sample and mobile phase, the adsorbed  $\text{Ag}^+$  can well desorbed from AgNPs and DOM, and then be separated effectively from AgNPs. Under the above conditions, AgNPs and  $\text{Ag}^+$  in the sample can be well separated in 5 min. Then the  $\text{Ag}^+$  in sample was quantified according to  $\text{Ag}^+$  standard and the concentration of AgNPs was obtained by subtracting the  $\text{Ag}^+$  from the total Ag, which was determined directly by ICP-MS after digestion (Zhou et al., 2014). The spiked recovery of  $\text{Ag}^+$  in 30 mg L $^{-1}$  DOM solution of this LC-ICP-MS method was  $98.7 \pm 0.6\%$ .

## 3. Results and discussion

### 3.1. Reduction of $\text{Ag}^+$ by $\text{Fe}^{2+}$

To probe the possible reduction of  $\text{Ag}^+$  by  $\text{Fe}^{2+}$ , the reaction of  $\text{Ag}^+$  and  $\text{Fe}^{2+}$  under simulated irradiation was monitored by UV-vis spectroscopy. As shown in Fig. 1A, a small absorption peak was evident at about 410 nm at 0.5 h, which was ascribed to the surface plasmon resonance (SPR) of AgNPs (Chinnapongse et al., 2011). The SPR peak enhanced over time from 0.5 to 2 h, indicating the further formation of AgNPs. However, the SPR peaks further broaden and shift to longer wavelength at 4 h-8 h, which was ascribed to the formation of AgNP aggregates (Yin et al., 2012) due to the absence of capping agent. Considering the relatively lower concentration of

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