1 Development of a filter-based method for detecting silver nanoparticles
2 and their heteroaggregation in aqueous environments by
3 surface-enhanced Raman spectroscopy

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Abstract

The rising application of silver nanoparticles (AgNPs) and subsequent release into aquatic systems have generated public concerns over their potential risk and harm to aquatic organisms and human health. Effective and practical analytical methods for AgNPs are urgently needed for their risk assessment. In this study we established an innovative approach to detect trace levels of AgNPs in environmental water through integrating a filtration technique into surface-enhanced Raman spectroscopy (SERS) and compared it with previously established centrifuge-based method. The purpose of filtration was to trap and enrich salt-aggregated AgNPs from water samples onto the filter membrane, through which indicator was then passed and complexed with AgNPs. The enhanced SERS signals of indicator could reflect the presence and quantity of AgNPs in the samples. The most favorable benefit of filtration is being able to process large volume samples, which is more practical for water samples, and greatly improves the sensitivity of AgNP detection. In this study, we tested 20 mL AgNPs-containing samples and the filter-based method is able to detect AgNPs as low as 5 $\mu\text{g/L}$, which is 20 folds lower than the centrifuge-based method. In addition, the speed and precision of the detection were greatly improved. This approach was used to detect trace levels of AgNPs in real environmental water successfully. Meanwhile, the heteroaggregation of AgNPs with minerals in water was reliably monitored by the new method. Overall, a combination of the filtration-SERS approach provides a rapid, simple, and sensitive way to detect AgNPs and analyze their environmental behavior.

Keywords: Silver nanoparticles, SERS, Filtration, Water samples, Heteroaggregation

Capsule

We developed an innovative SERS approach that can rapidly, sensitively and reliably detect trace levels of AgNPs in environmental waters and monitor their heteroaggregation with minerals.

Introduction

Widespread application of silver nanoparticles (AgNPs) has caused extensive discussion on their benefits and side effects to our society and environment. The form of NPs, which possess small sizes and large surface area to volume ratios, not only improves the inherent properties of metal silver, such as electrical conductivity, thermal conductivity and reflectivity, but also confers silver new merits including antimicrobial activity and surface plasmon resonance (SPR) (Jain et al., 2008; Kim et al., 2007; Wijnhoven et al., 2009). Due to these special properties, AgNPs are of significant interest to manufacturers of antimicrobial products, electronics, catalysts and SPR-related techniques (Wijnhoven et al., 2009). However, during production, distribution, application and disposal of these products, AgNPs are being released into environmental systems and potentially pose risks to living organisms (Benn et al., 2010; Benn and Westerhoff, 2008; Froggett et al., 2014; Gottschalk and Nowack, 2011; Kulthong et al., 2010; Quadros and Marr, 2011; Quadros et al., 2013). Plenty of studies have reported the toxicity of AgNPs to bacteria, plants, animals and human cells (Bohmert et al., 2014; Kulthong et al., 2010; Ma et al., 2010; van Aerle et al., 2013), indicating that AgNPs may endanger aquatic organisms when released into water environments (Fabrega et al., 2011). Up to date, it has been reported that more than 110 officially registered silver containing pesticides are used for medical, agricultural, environmental and home purposes (Bergeson, 2010). Many of them consist of nanosilver, which may leach out during application and adversely affect aquatic ecosystem (Nowack et al., 2011). To evaluate the environmental impact of AgNPs, effective and reliable analytical techniques for AgNPs are a prerequisite.

83 For environmental water samples, generally speaking, the volume of sampling is not restricted.
84 In fact, high volume of water samples (20-100 mL) are often required for representative results
85 (U.S. Environmental Protection Agency, 1994). However, many of the current techniques for
86 NPs detection and characterization, such as scanning electron microscopy (SEM), transmission
87 electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS), can only look at
88 very small volume of samples. Besides, AgNPs are known to be very active and transitive in
89 environmental waters (Levard et al., 2012; Yu et al., 2013). However, many techniques such as
90 graphite furnace atomic absorption spectrometry (GFAA), inductively coupled plasma optical
91 emission spectrometer (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS),
92 are unable to differentiate AgNPs from other silver species. Single particle ICP-MS (sp-ICP-MS)
93 is a promising technique to identify AgNPs from other silver species, but it is inaccurate to detect
94 AgNPs smaller than 30 nm and the sizing resolution can be low (Mitrano et al., 2012a, 2012b).
95 Furthermore, as far as we know, none of current techniques for analyzing AgNPs can be applied
96 to on-site detection, which is however desirable for providing the most reliable information of
97 AgNPs in natural environments. Additional challenge for AgNP detection in environmental water
98 samples is the extreme low concentration. Models based on the life cycle of AgNP-containing
99 products showed that the levels of nanosilver were 0.09-0.43 ng/L in the surface water of the
100 U.S., and 0.59-2.16 ng/L in the surface water of Europe (Gottschalk et al., 2009). This highlights
101 the requirement of highly sensitive techniques for detecting AgNPs in environmentally relevant
102 levels.
103 Recently, an innovative method based on surface-enhanced Raman spectroscopy (SERS) was

established to detect AgNPs in antimicrobial consumer products (Guo et al., 2015). The SERS technique proved to be effective to differentiate AgNPs from their bulk counterparts and other silver species owing to the specifically induced SERS effect by AgNPs. However, the sample preparation in that method requires high-speed centrifugation, which is not practical for large volume of samples and inconvenient for on-site detection. In addition, the sensitivity of that method is 0.1 mg/L, which is not satisfactory for real application in water samples and may be improved by optimizing the sample preparation.

Facing these issues, here we developed a new approach through incorporating membrane filtration technique into the SERS method. Membrane filtration has wide applications in water treatment and air quality control. It allows large volume of samples to pass through for enrichment in a short time. The filtration techniques are widely used to remove inorganic or organic contaminants during waste water treatment (Brandhuber and Amy, 1998; Geise et al., 2010; Meng et al., 2001; Van Der Bruggen and Vandecasteele, 2003). They are also preferably used for testing microbiological pollutants in water (Geise et al., 2010; U.S. Environmental Protection Agency, 1978; Van Der Bruggen and Vandecasteele, 2003), or particulate matter in the air (Alzona et al., 1979; Marcazzan et al., 2001; Schauer et al., 2003). Additional benefits include low-price and portability. In this study, we utilized a simple filter syringe to enrich the AgNPs upon adding salts. Ferbam was used as an indicator of AgNPs based on our previous study (Guo et al., 2015). Comprehensive evaluations of the filtration-SERS method for detecting AgNPs were made through comparison with previously established centrifugation-SERS method. Influencing factors of AgNP detection, such as signal variation, sensitivity, flexibility for

adjusting sample size, and easiness for on-site detection, were prudently compared between the filter-based method and the centrifuge-based method. Meanwhile, the potential of the filtration-SERS method to screen and detect heteroaggregated AgNPs from free AgNPs in the presence of minerals was tested. To the best of our knowledge, this is the first time that the filtration-SERS method was developed and evaluated for examining the presence and behavior of AgNPs in aqueous environments.

Materials and Methods

Materials

Millipore PVDF filter membranes with a diameter of 13 mm and pore sizes of 0.1 μm , NORM-JECT plastic syringes, ferbam, CaCl_2 and AlCl_3 were all obtained from Fisher Scientific. Filter holders with a diameter of 13 mm was purchased from Cole-Palmer (Vernon Hills, IL). AgNPs (20 mg/L, 60 nm and citrate coated) was obtained from NanoComposix (San Diego, CA). Pond water collected from University of Massachusetts Amherst in April, 2015 was spiked with AgNPs to simulate AgNPs-contaminated environmental water. Inorganic carbon content and total organic carbon content (TOC) in the pond water sample were determined by a total carbon analyzer (Shimadzu, TOC-L). Electrical conductivity (EC) and pH of the water sample were measured by a conductivity/pH meter (Fisher Scientific, XL200). In order to quantify the total solid concentration, 50 mL of water sample was added into a clean dish and dried in an oven at 100 $^{\circ}\text{C}$ for 24 h. The total solid concentration was obtained based on the mass difference between the clean dish and the dried dish with residue.

Methods

The filtration approach utilizes a simple syringe filter system to capture aggregated AgNPs in the sample. To avoid the formation of bubbles and make the filtration process easier, the filter membrane was placed in a 1:1 water/ethanol solution for 5-10 min prior to filtration (Yu and White, 2012). The tested sample was firstly mixed with 1 M CaCl_2 or AlCl_3 at a volume ratio of 100: 1 for a period of time to aggregate AgNPs. Dynamic light scattering (DLS, Brookhaven, 90Plus) was used to monitor the hydrodynamic diameter change of AgNPs over time. For CaCl_2 , the average size of AgNPs increased from 66.0 ± 0.6 nm (0 min) to 79.2 ± 1.1 nm (10 min). At 15 min, the average size (91.9 ± 0.7 nm) was still lower than 100 nm. However, the majority of AgNP aggregates became bigger than 100 nm at 20 min (Table S2 and Figure S3). Therefore, 20 min was used for all the samples with CaCl_2 as aggregating salt. In order to compare CaCl_2 with AlCl_3 , 20 min time was also used for the samples with AlCl_3 , which can also ensure that AgNP aggregates are larger than 100 nm (Table S2 and Figure S3). To show the heteroaggregation of AgNPs with minerals, no aggregating salt was added. Instead, 250 mg/L goethite (Aldrich Chemical Company, Inc.) or kaolinite (Fluka Chemical Corp.) was well mixed with AgNPs without further incubation. The sample was then filtered through the membrane with pore sizes of 0.1 μm . Further, 2 mL ferbam (10 mg/L) was slowly filtered through the same membrane. Ferbam functions as an indicator of AgNPs because of the enhanced characteristic signals upon mixing with AgNPs (Narayanan et al., 1992; Saute and Narayanan, 2013) and strong binding affinity with AgNPs via multiple sulfur atoms, which can resist the interference from other components in the sample. The chemical structure and Raman band assignments of ferbam are

presented in Figure S1 and Table S1. After filtration of ferbam, the membrane was removed and air dried on a microscopic slide for Raman analysis. A DXR Raman microscope (Thermo Fisher) with a 780 nm laser was used for Raman measurements. Raman spectra were collected using a 10 × confocal microscope objective with 3 μm spot diameter and 5 cm⁻¹ spectral resolution with an output power of 5 mW as well as a 50 μm slit width for 2 s integration time.

The centrifugation-SERS method was performed according to our previous study (Guo et al., 2015). Briefly, different concentrations of AgNPs were incubated with ferbam (10 mg/L) in a volume ratio of 3:17 on a 24 rpm Nutating mixer (Fisher Scientific) for 45 min at room temperature. Centrifugation (10 000 rpm, 5 min) was followed to deposit the AgNPs-ferbam complexes to the bottom. The precipitates were then sampled on a gold slide and dried in a fume hood. Detection of AgNPs by SERS was conducted using the same method as filtration-SERS method.

Statistical analysis

SERS spectral data were analyzed using TQ analyst software (version 8.0, Thermo Scientific). Ten randomly selected spectra within each membrane were averaged to obtain the final spectrum. One example showing the low variance across the ten data points and the good representativeness of the averaged spectrum is provided in Figure S4.

Results and Discussion

Evaluation of the quantitative ability, sensitivity and signal variation of the filter-based method

Figure 1A shows the dependence of SERS intensity on AgNP concentration (1.5 mL). The signals increased with AgNP concentration increasing from 0 mg/L to 1 mg/L, which indicates good capture efficiency using the membrane. We further built a linear curve between signal intensity at 1387 cm^{-1} and AgNP concentration (Figure 1B), which shows a great quantitative potential of the filtration-SERS method for AgNPs. Based on the signal-to-noise ratio of 3 (Chandran and Singh, 2007), the detection limit was 0.025 mg/L, much lower than the detection limit (0.1 mg/L) of the centrifugation-SERS method. Moreover, compared to the centrifugation-SERS method, the filtration-SERS method produced higher signal intensity at the same concentration of AgNPs (Table 1, Figure S5). In addition, the signal variation was significantly reduced as compared to the centrifuge-based method (Table 1, Figure S5), suggesting better quantitative ability of the filter-based method.

Figure 1. Concentration-dependent SERS response to AgNPs via the filtration-SERS method. SERS spectra (A) and linear relationship between signal intensity and AgNP concentration (B). The error bars are representative of the standard errors of five equivalent SERS measurements.

Table 1. Comparison of signal intensity and data variation between the filtration-SERS method and the centrifugation-SERS method.

Method	Concentration of AgNPs (mg/L)	Signal intensity	Standard deviation	Coefficient of variation
Filtration-SERS	1	11269	248.8	0.022
	0.5	6478	210.4	0.032
	0.1	528	33.5	0.063
Centrifugation-SERS	1	896	308.4	0.344
	0.5	360	219.4	0.610
	0.1	31	3.9	0.127

In order to examine if the aggregated AgNPs were all trapped on the membrane, we analyzed AgNPs in the filtrate of 1 mg/L AgNPs using the filtration-SERS method again and no signals were detected, which means the concentration of remaining AgNPs in the filtrate is less than 0.025 mg/L according to the detection limit shown in Figure 1A. Therefore, at least 97.5% AgNPs were trapped on the membrane and detected by filtration-SERS method. The mean diameter and size distribution of AgNPs aggregated by CaCl_2 (Table S2 and Figure S3) also showed that most AgNP aggregates were larger than 100 nm, which are consistent with the SERS results. In contrast, the centrifugation-SERS method only used several micro liters of deposited AgNPs for Raman measurements, which could not ensure the majority of AgNPs were included in the analysis.

Evaluation of the sample volume adjustability of the filtration-SERS method

We further evaluated the performance of the filtration-SERS method for detecting AgNPs at different volumes. In Figure 1A, 1.5 mL of 50 $\mu\text{g/L}$ AgNPs were tested. Although the enhanced signals of ferbam can be identified compared with the control, the signals were very weak and

the noises from the membrane were noticeable. As we increased the volume from 1.5 mL to 3 mL, 6 mL and 9 mL, the signal intensities were progressively increased (Figure 2), indicating that the sensitivity could be improved by increasing the sample volume. Also, this result demonstrates another advantage of the filtration-SERS method over the centrifugation-SERS method: flexible adjustability of sample volume.

Figure 2. SERS spectra of different volumes (9, 6 and 3 mL) of AgNPs (50 µg/L) using the filtration-SERS method.

We further explored the possibility to take the advantage of sample volume adjustability to improve the sensitivity of filtration-SERS method. In the first place, we used CaCl_2 as aggregating agent for AgNPs at 10 µg/L and 5 µg/L as we did for high concentrations (≥ 50 µg/L), but no enhanced ferbam signals were detected for both concentrations even using a higher

sample volume (20 mL). It is possible that CaCl_2 we used was unable to aggregate AgNPs at such low concentrations. As a result, AgNPs could not be trapped onto the membrane and no enhancement effect was exhibited. Based on the Schulze–Hardy rule, colloid stability dramatically decreases with the increase of counter-ion valence in coagulating electrolytes. Because AgNPs used in this study are negatively charged, the cation valence in electrolytes plays a dominant role in the aggregating effect. As shown in Table S2 and Figure S3, AgNPs aggregated by AlCl_3 had bigger sizes than those aggregated by CaCl_2 under the same conditions. Therefore, we replaced CaCl_2 with AlCl_3 . Notably, AgNPs were detected at both concentrations (10 $\mu\text{g/L}$ and 5 $\mu\text{g/L}$) when high sample volume (20 mL) was used (Figure 3). Therefore, for low concentrations of AgNPs, cations of higher valance should be used to ensure that AgNPs are aggregated enough to be trapped onto the membrane. In this manner, the sensitivity of the filtration-SERS method can be greatly increased at high volumes.

Figure 3. SERS spectra of 20 mL of AgNPs (10 and 5 µg/L) using the filtration-SERS method.

Validation of filtration-SERS method to detect AgNPs in environmental water

To demonstrate the capability of the filtration-SERS method to detect AgNPs in environmental water samples, we spiked AgNPs into a locally collected pond water sample to simulate AgNPs-contaminated natural water. Figure 4 showed the detection of 10 µg/L AgNPs with a sample volume of 20 mL and AlCl_3 as aggregating salt. Evidently, the filtration-SERS method is feasible to detect AgNPs even in the presence of matrix substances (e.g., natural organic matter, metal cations and inorganic anions, Table S3) in the water. Further improvement of sensitivity may be realized using even higher volume of samples, and a vacuum-based filter system would be preferred for rapid and effective operation.

Figure 4. SERS spectra of 20 mL of AgNPs (0 and 10 µg/L) in pond water using the filtration-SERS method.

Application of filtration-SERS method to study the heteroaggregation of AgNPs with minerals in aqueous environment

Filtration-SERS method can have great potential to be used as a convenient and reliable technique to study the heteroaggregation of AgNPs in aqueous environments. Minerals are ubiquitous and abundant in aqueous environments so it is likely that minerals will interact with NPs and consequently change their mobility, stability and transport. It was reported that negatively charged minerals could lead to the destabilization of positively charged TiO_2 nanoparticles via heteroaggregation in aqueous environment (Wang et al., 2015; Zhou et al., 2012). The dominant force of heteroaggregation was demonstrated to be electrostatic interaction

(Wang et al., 2015; Zhao et al., 2015; Zhou et al., 2012). Negatively charged AgNPs, such as citrate-AgNPs, are thus expected to strongly adsorb onto positively charged minerals through electrostatic attraction, or stay dispersed due to repulsive interaction with negatively charged minerals, both of which probably influence the transport of AgNPs in the environment. For minerals of pH-dependent surface charge, the heteroaggregation of AgNPs may be influenced by solution pH. For example, goethite can be negatively or positively charged depending on solution pH (Zhao et al., 2015), which may affect the interactions with AgNPs. However, accurate measurement of the heteroaggregation of AgNPs is still a challenge. Routine techniques to analyze the aggregation of AgNPs, such as DLS and UV-vis can be readily interfered by the presence of minerals. Centrifugation-SERS can specifically detect AgNPs, but it is difficult to differentiate heteroaggregated AgNPs from free AgNPs through centrifugation. Due to the limitation of current techniques in direct measurement of heteroaggregation, Quik et al. used sedimentation data to estimate heteroaggregation by using models (Quik et al., 2014), which is indirect and may lead to inaccuracy. Therefore, innovative methods for determining heteroaggregation behavior of AgNPs are needed. Here, we demonstrate the effectiveness of the filtration-SERS method to specifically detect heteroaggregated AgNPs on mineral surface through membrane separation of mineral-sorbed AgNPs from dispersed AgNPs. In this study, we utilized the filtration-SERS method to investigate the heteroaggregation of AgNPs with two types of minerals: goethite and kaolinite. Goethite is an iron oxyhydroxide with ZPC around 8.5-9.0 (Zhao et al., 2015). Kaolinite is a phyllosilicate with ZPC around 4.0 (Wei et al., 2014). They are both passed through a 100-mesh (149- μ m) sieve with final size larger than the

membrane pore size. As shown in Figure 5A, the mixture of AgNPs and goethite produced higher signals while AgNPs and kaolinite produced weaker signals than AgNPs alone at pH 7. This is because goethite is positively charged at pH 7, which can electrostatically adsorb negatively charged AgNPs, leading to more AgNPs trapped on the membrane. On the other hand, kaolinite is negatively charged at pH 7 and the repulsive force makes negatively charged AgNPs too dispersed to be withheld by the membrane. The filtration-SERS method can not only reflect the different heteroaggregation behaviors of AgNPs with different minerals, but also show the pH effect on the interaction of AgNPs with goethite. A higher pH 11 led to lower SERS signals compared with pH 7 (Figure 5B), which is reasonable because goethite is negatively charged at pH 11 and repulsion dominates the interaction of goethite with AgNPs. Overall, the filtration-SERS method is a simple, rapid and accurate approach to measure the heteroaggregation of AgNPs with minerals.

Figure 5. Filtration-SERS shows different heteroaggregation behaviors of AgNPs with different minerals (goethite vs. kaolinite) at pH 7 (A) or goethite at different pHs (B).

Detailed comparison of filtration-SERS method and centrifugation-SERS method

A crucial step of detecting AgNPs at low concentrations is to enrich them into a small amount of sample so the concentrated AgNPs can enhance the signals of ferbam, which in turn signify the presence of AgNPs. We used two ways to achieve this: centrifugation and filtration. The centrifuge method involved long time incubation and high-speed centrifugation, which is time-consuming and requires a high-speed centrifuge (Guo et al., 2015). On the other hand, the filtration method is based on a syringe, a membrane holder and membranes, which is fast, easy to operate, and instrument-free. As shown in Table 2, in addition to the advantages we mentioned above like high sensitivity, precision, and flexibility, the filtration-SERS method has great potential for on-site detection of AgNPs if a portable Raman instrument is used. Another potential application of the filtration-SERS method is the detection of atmospheric AgNPs released in the life cycle of consumer products, and further investigation is needed. So far, the centrifuge-based method has been used to detect AgNPs in antimicrobial products (Guo et al., 2015), spinach juice and environmental water (Figure S6). Although the filter-based method may be less favorable for detecting AgNPs in complex matrices (e.g., antimicrobial products and spinach juice) due to the clogging of membrane pores by sample matrices, it is more advantageous than the centrifuge-based method for detecting AgNPs in samples of large volume as well as their heteroaggregation in environmental water.

Table 2. Detailed comparison of the centrifugation-SERS and the filtration-SERS method.

Parameter	Centrifugation-SERS	Filtration-SERS
Time	60 min at least	~25 min
Signal intensity	Low	High
Signal variation	High	Low
Sensitivity	0.1 mg/L	0.005 mg/L
On-site detection	Difficult	Easy
Adjustability	Low	High
Application	Samples of low volume	Samples of large volume, heteroaggregation

Conclusion

We developed a rapid, simple, sensitive, flexible and convenient method to detect trace levels of AgNPs in environmental water through combining filtration with SERS technique. Filtration was used to concentrate AgNPs upon adding salt from environmental water onto a filter membrane. SERS is able to specifically detect trapped AgNPs on the membrane with the aid of ferbam as an indicator. We demonstrated the great advantages of the filtration-SERS method over the centrifugation-SERS method in detection of AgNPs in environmental water. The developed method has significant value for economically conducting reliable survey of AgNPs in environmental waters, which is of critical importance for risk assessment of AgNP exposure. Moreover, filtration-SERS is feasible to analyze the heteroaggregation behavior of AgNPs with minerals, which can facilitate the evaluation of AgNP fate and transport in aqueous environment.

Acknowledgements

This study is supported by USDA-NIFA 2015-67017-23070 and USDA-NIFA Hatch program (MAS 00475).

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