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Practical SERS method for assessment of the washing durability of textiles containing silver nanoparticles

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ABSTRACT

The popular use of silver nanoparticles (Ag NPs) in the production of commercial odor-control and antibacterial textile products has raised questions about their washing durability. Poor durability not only deteriorates product performance but also results in unknown amounts of Ag NPs leaching into sewage- and water-treatment systems. Therefore, it is necessary to have a quick and easy method for detecting Ag NPs in washing solutions for assessment of washing durability. In this study, we have developed a practical surface-enhanced Raman spectroscopy (SERS) method for measuring the concentrations of Ag NPs in water and a detergent solution. To improve the sensitivity and reproducibility of SERS signals from the complexation of an indicator molecule (ferric dimethyl-dithiocarbamate, in this study) with NPs, the "coffee ring effect" was utilized. The active SERS "hot spots" in the aggregated NPs along the coffee ring effectively intensified the signature SERS response, even with NPs of about 10 nm in diameter and a concentration as low as 0.01 mg/L. The linear relationships between SERS intensity and Ag NP concentration ($R^2 > 0.99$) successfully quantified the amount of Ag NPs released from Ag NP-treated cotton fabrics during washing as well as other Ag speciation formed in a detergent solution.

KEYWORDS: *Silver nanoparticles; Surface-enhanced Raman spectroscopy; Coffee ring; Cotton; textiles; Wash durability; indicator*

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1. Introduction

In reaction to constantly emerging new pathogens, pressure to develop more effective and persistent antibacterial consumer products has increased. In particular, textiles, which come in direct contact with skin during normal use, can be a potential vehicle for transmitting infection. According to a report published by ReportBuyer, the global antibacterial textiles market is forecasted to grow from USD 9.5 billion in 2019 to USD 12.3 billion in 2024.[1] In recent years, making antibacterial textiles employing silver nanoparticles (nanosilver or Ag NPs) has been increasingly popular because of their powerful biocidal activity.[2] Ag NPs, with a high surface-area-to-volume ratio, can effectively release antibacterial Ag ions,[3, 4] and Ag NPs can penetrate and damage bacterial cells.[5-7] Commercially available Ag NP-containing textile products, which inhibit the growth of odor-causing bacteria and pathogenic microorganisms, include socks, shirts, sportswear, underwear, blankets, and medical textiles. This proliferating use of Ag NPs have caused public concern over the potential risks of their environmental release, prompting intensive studies of their washing durability.[8-17] These studies have agreed that both laboratory-prepared and commercial textiles lost a significant amount of Ag NPs during laundering. Up to 20%–30% of the total Ag in the textiles were detached in the first washing,[10-12] and 87% were washed off during five simulated home laundering cycles.[8]

Textiles containing Ag NPs can release ionic and particulate Ag during washing.[10] The NPs slowly dissolve in an aqueous environment, releasing positive Ag ions through the oxidation of metallic Ag.[18] The particulate Ag detached from the textiles tends to agglomerate into larger particles. A significant amount of particles greater than 0.45 μm were observed in rinsing and washing solutions.[9-12, 14] To differentiate ionic Ag and particulate Ag and size-fractionate particles in washing solutions, most researchers have used filtration.[9-12, 14, 16, 17] The Ag that passed through a membrane with a size of 3 kDa was assumed to consist of Ag ions. The amount of corresponding Ag is generally measured using inductively coupled plasma mass spectrometry (ICP-MS). This method, however, is likely to lose Ag during filtration and takes a long sample preparation time because it requires the digestion of the sample.

More importantly, it is unable to differentiate Ag NPs from other Ag species. According to analyses using electron microscopy and energy dispersive X-ray spectrometry, in addition to metallic Ag, other Ag species such as Ti/Si-AgCl nanocomposites, AgCl NPs, and Ag_2S NPs coexisted in the washing solutions.[12, 14] Such transformations into various Ag species were considered to have resulted from the interactions with compounds in the detergent solutions. Having reliable information regarding the release of Ag NPs by identifying and quantifying Ag NPs in washing solutions is essential for evaluating the washing durability of Ag NP-treated textiles and reducing the uncertainties related to their environmental exposure.

Previous studies[19-23] showed that SERS can be employed to develop methods to identify and quantify Ag NPs. These methods are based on the enhancement of the Raman signal of the analyte by electromagnetic enhancement induced by localized surface plasmon resonance of NPs and chemical enhancement induced by the charge transfer between the analyte and NPs. Using Raman indicator molecules, which bind to the surfaces of Ag NPs, it was possible not only to detect Ag NPs with distinct coatings and in multiple sizes and concentrations but also to differentiate Ag NPs from other Ag species such as silver ions, silver chloride, and silver bulk particles.[19] This SERS method was effectively applicable for detecting Ag particles ranging from 20 to 200 nm. Its applicability was verified with Ag NPs of different surface coatings (polyvinylpyrrolidone and citrate) and by measuring the concentrations of Ag NPs in commercial antimicrobial products (throat spray, nasal spray, antifungal spray, and antibacterial hydrogel) without removing matrices.[19] Despite its reliability, simplicity, and fastness, the method of directly conjugating the indicator molecule in a colloidal solution has an optimum particle size for enhanced signal intensity, which was 60-100 nm.[19]

To improve the sensitivity and reproducibility of the SERS method for smaller NPs, here we developed a new approach using the "coffee ring effect"[24] to create active SERS sites, i.e., "hot spots". The coffee ring effect involves the formation of a ring-like deposit along the perimeter of a drop of coffee when the drop dries on a solid surface. This characteristic pattern was attributed to the capillary flow induced by the differential evaporation rates across the drop.[24] This phenomenon carries nearly all the

dispersed material to the edge. Wang et al.[25] employed the coffee-ring effect for constructing SERS substrates. They added polyvinyl alcohol (PVA) in the solution containing Ag NPs and an analyte molecule in order to aggregate Ag NPs before depositing the solution on the hydrophobic surface of a silicon wafer. The coffee-ring formation was strongly dependent on the concentration of PVA. Other aggregating agents, such as $CaCl_2$ and $AlCl_3$ for Ag NPs,[20] and various chloride salts ($MgCl_2$, $CaCl_2$, KCl, and NaCl)[26] for Au NPs, have been used. The aggregated NPs can produce higher SERS signals than individual NPs because the electromagnetic field in the junctions between NPs is intensified.[27-29] In this study, we employed the coffee-ring effect, without using any aggregating agents, for inducing the self-assembly of Ag NPs prior to the conjugation of an indicator molecule. This method involves a two-step spotting method—Ag NPs followed by an indicator—to maximize the number of hot spots by controlled capillary flow. Iron (III) *tris*(dimethyldithiocarbamate) (ferbam) was selected as an indicator molecule based on the previous study.[19] Ferbam has strong interactions with Ag NPs through thiol groups and forms complexation, which produces a characteristic SERS fingerprint spectrum.[19] The Raman signals and their reproducibility by this method were compared with those of the previously published method that conjugates ferbam with individual Ag NPs prior to deposition. Relationships between Raman signal intensity and the concentrations of Ag NPs in DI water and a detergent solution were established. Finally, the effectiveness and sensitivity of the new approach was demonstrated by identifying and quantifying the Ag NPs in washing solutions obtained after consecutive launderings of Ag NP-treated cotton fabrics.

2. Experimental

2.1. Materials

Mechanically pre-cleaned raw white cotton fiber was acquired from T. J. Beall (Greenwood, MS). Bleached and desized cotton print cloth (98 g/m^2) was purchased from Testfabrics, Inc. (West Pittston, PA). Silver nitrate ($AgNO_3$, 99.9 %) was purchased from J. T. Baker. Sodium hydroxide (NaOH, 97 %), ammonium hydroxide solution (NH_4OH, 28–30 %), and L-ascorbic acid ($C_6H_8O_6$, 99 %) were purchased from Sigma-Aldrich (St. Louis, MO). Iron (III) *tris*(dimethyldithiocarbamate) ($C_9H_{18}N_3S_6Fe$, ferbam) was

purchased from TCI America (Portland, OR). All materials were used as received. Deionized (DI) water (18.0 MΩ/cm) and Milli-Q water were used.

2.2. Synthesis and treatment of Ag NPs

The synthesis of Ag NPs was adapted from a previously published method[30] but using raw cotton. This method utilizes a swollen cotton structure in an NaOH solution to *in situ* produce Ag NPs. The unique surface nature of the raw cotton allowed the effective formation of Ag NPs not only inside the fiber but also on the surface of the fiber. Ag NPs formed on the fiber surface were collected by agitating the fabric in DI water at 40 ± 1 °C for 6.5 hours. The obtained dark yellow solution was filtered using Whatman No. 5 filtration paper to remove any fiber fragments. Water-soluble impurities were removed by centrifugation (Ultracentrifuge, Hitachi) at 50,000 rpm for 30 min. The sedimented NPs were redispersed in DI water. For the treatment of Ag NPs onto a fabric, a bleached and desized cotton print cloth was cut into a 5 × 10 cm rectangle, immersed in the a 30 mL Ag colloidal solution at a concentration of 50 mg/L, and passed through a laboratory padder (Werner Mathis) at a pressure of 0.3 MPa and a padder speed of 2 m/min. The treated fabric was air-dried. The amount of Ag NPs based on the dry weight of the fabrics was determined to be 40 ± 5 mg/kg by ICP-MS.

2.3. Consecutive washings in DI water and a detergent solution

Washing in the laboratory machine, a Launder-Ometer (M228-AA, SDL Atlas LLC), was carried out following AATCC Test Method 61-2007: Colorfastness to Laundering: Accelerated with modification. A stainless-steel canister (75 ± 5 mm diameter, 125 ± 10 mm height, 550 ± 50 mL) filled with 400 mL of water was preheated to 40 ± 1 °C in the washing machine. A fabric sample (5 × 5 cm) was placed in a 50 mL polypropylene bottle containing 15 mL of DI water or a detergent solution and 10 glass balls (5 mm in diameter). The detergent solution was prepared using a laundry detergent of Tide® (Procter & Gamble Co.) with 0.15% w/v in DI water. The glass balls were used to simulate the friction of home laundering. The closed bottle was placed in the preheated water in the canister and rotated at 40 ± 1 °C at a constant rate of 40 ± 2 rpm for 45 min. This procedure simulated five home laundry cycles and was repeated for up

to 50 cycles. After washing, the fabric was removed from the bottle, and the washing solution was collected for the analyses of Ag NPs leached from the fabric.

2.4. Characterization of Ag colloidal and washing solutions

UV/Vis spectra were obtained for a wavelength range of 220–800 nm using a UV/Vis/NIR spectrometer (ISR-2600, Shimadzu). A quartz cuvette with a 1 cm long optical path was used. A micrograph of Ag NPs was obtained using a transmission electron microscope (TEM, JEOL 2010) operating at 200 kV. A drop of a purified Ag colloidal solution was placed on a carbon-film-coated copper grid and dried before being used for observation under the TEM. The average particle size and the size distribution of Ag NPs were obtained by analyzing the obtained micrographs using Image J software15. About 800 particles were measured. The concentration of Ag NPs was measured using an inductively coupled plasma mass spectroscope (ICP-MS, Agilent 7500ce) and filtration. Colloidal and washing solutions may contain Ag ions dissolved from Ag NPs. To determine the concentration of Ag ions, the solution was filtered using a centrifugal unit (Sartorius Stedim Vivaspin®6, Sartorius AG) equipped with a polyethersulfone membrane at a molecular weight cut-off of 3 kDa (ca. 1 nm). The concentrations of Ag in the solution before and after filtration were analyzed with ICP-MS, and the difference between the two concentrations was considered along with the concentration of Ag NPs. The ICP-MS analysis was conducted in the ICP-MS Metals Laboratory at the University of Utah. A 4 mL solution was dried down and refluxed for 1 hour with 2 mL of 16 M nitric acid on a hot plate and dissolved in 1 mL of 0.8 M nitric acid with 10 ppb of indium. The resulting solution was analyzed with an external calibration curve obtained using a silver single-element standard (Inorganic Ventures). The Ag concentration in cotton fabrics was also analyzed using ICP-MS. Approximately 0.05 g of the sample was treated with 2 ml of 16 M nitric acid (Trace Metal Grade) and digested in a Milestone Ethos Microwave System. The digest was diluted by weight 1:10, and 10 ppb of indium was added. The digested solution was analyzed with an external calibration curve.

The contact angles of DI water and detergent solution droplets on the gold slide were measured using a contact angle analysis equipment (VCA Optima XE, AST Products, Inc.). A 1 μL drop was syringed onto the slide. The image of the droplet on the slide was captured as a function of time and analyzed to measure a contact angle. The average of three measurements was presented.

2.5. SERS method for the analysis of Ag NPs

A schematic of the conjugation of ferbam onto Ag NPs is shown in Fig. 2. The indicator solution was prepared by dissolving 5 mg of ferbam in 5 mL of acetone (1000 mg/L). This stock solution was diluted with Milli-Q water to a concentration of 20 mg/L. An Ag colloidal solution (400 μL) was centrifuged at 15,000 rpm for 20-40 min, and a colorless supernatant liquid (370 μL) was removed. The washing solution was diluted with DI water before the centrifugation. After the remaining solution (30 μL) was ultrasonically agitated for 15 min, a droplet (4 μL) of the solution was spotted by a micropipette on a gold slide (BioGold™ microarray slide, Erie Scientific LLC) and dried at room temperature. Next, a bigger droplet (8 μL) of the aqueous solution of ferbam was spotted on top of the coffee ring of Ag NPs and dried at room temperature. The ferbam solution was spotted immediately after the coffee ring of Ag NPs was formed. The coffee ring of Ag NPs conjugated with ferbam on the gold slide was observed using a digital microscope (KH-8700, Hirox) and a field emission scanning electron microscope (FE SEM, Hitachi 4800) operating at 3 kV. The dried sample was immediately analyzed using a Raman spectrometer (DXR2, Thermo Scientific). The instrumental settings were an excitation wavelength of 785 nm, output power of 5 mW, a 10X confocal microscope objective, a spot size of 1.9 μm, and a slit width of 50 μm. The long-wavelength excitation was used to avoid fluorescence interference from sample and to prevent the potential photodegradation of ferbam or photochemical transformation of Ag NPs resulting from intense irradiation. Each spectrum was a sum of 4 scans of 2 s integration time. Each measurement was collected by focusing the laser spot on the coffee ring of Ag NPs. At least 20 measurements were collected along the coffee ring, and the average spectrum was presented.

3. Results and discussion

3.1. SERS method using a coffee ring of Ag NPs

Fig. 1a shows the TEM micrograph of Ag NPs synthesized using raw cotton fiber. Most Ag NPs were quasi-spherical. The average diameter of the NPs based on about 800 particles was 10.2 ± 3.6 nm. As can be seen in the size histogram (Fig. 1b), particle size was monodispersed roughly following a Gaussian distribution. The UV/Vis spectra of Ag colloidal solutions with incremental concentrations show that Ag NPS exhibited surface plasmon resonance (SPR) at 417 nm (Fig. 1c). This characteristic SPR agrees with findings observed for spherical Ag NPs of similar size in other studies.[31-33]

Fig. 2 shows a schematic of the SERS method used to identify and quantify Ag NPs. This method utilizes the coffee-ring effect, which has been observed for various NP-dispersed solutions,[34-36] to enhance the Raman signal of an indicator (ferbam in this study) and its reproducibility. First, a droplet of the Ag colloidal solution was spotted on a gold slide and dried. Then a larger droplet of an aqueous solution of ferbam was positioned to cover the entire coffee ring of Ag NPs and dried. Fig. 3a shows the optical micrograph of the dried sample. A double ring consisting of the inner and outer rings formed by Ag NPs and ferbam, respectively, was observed. A magnified image of the inner ring shows that the thickness of Ag NP aggregation with 0.1 mg/L was about 6 μm. The particle assembly formed on the coffee ring was also confirmed by the corresponding FE SEM images taken at various magnifications (Fig. 4). Along these coffee rings, Raman spectra were collected. The inner ring exhibited the enhanced Raman signal of ferbam (Fig. 3b), but the spectra of the outer ring did not exhibit any distinct peaks (Fig. 3c). The noticeable enhancement of the Raman signal on the inner ring indicates that ferbam effectively conjugated with the assembly of Ag NPs on the coffee ring. The resulting Ag NP-ferbam complex enhanced the Raman signal of ferbam through the electromagnetic enhancement induced by localized surface plasmon resonance from NPs and chemical enhancement produced by charge transfer through the Ag-thiol groups between Ag NPs and ferbam.[19] The strongest SERS intensity was observed at 1381 cm^{-1},

which was assigned to the vibrational modes of ferbam: ν(C–N) stretching, ν(C=S) stretching, and $\nu(CH_3)$ symmetric deformation.[37] This peak was later used for the quantification of Ag NPs.

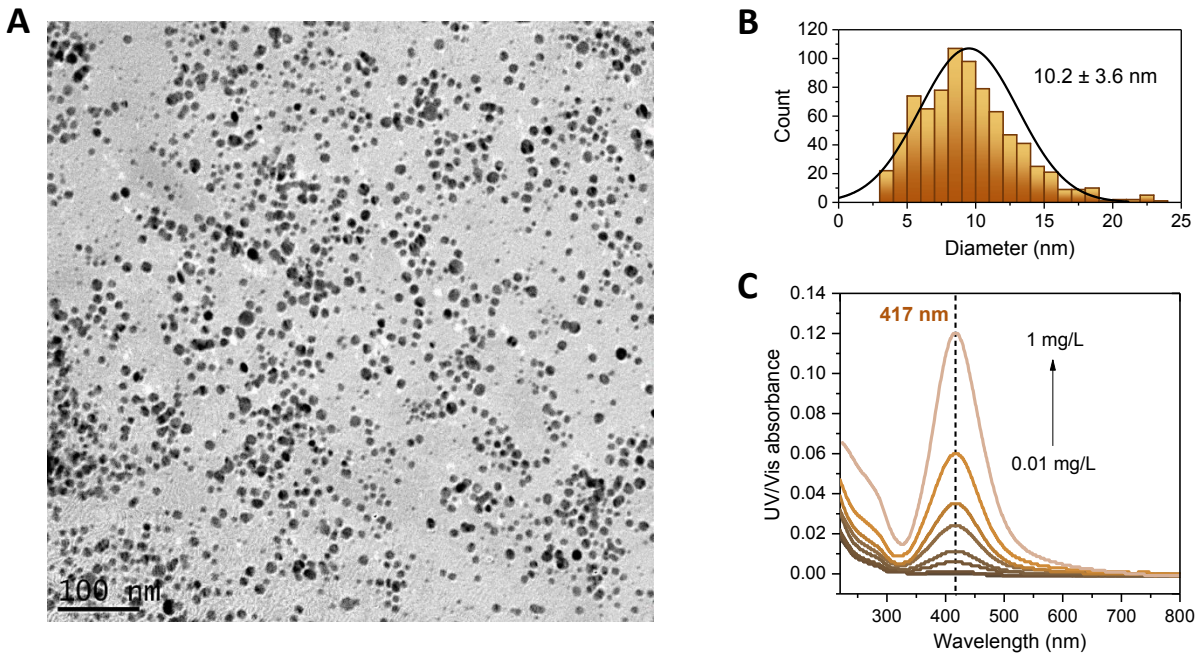

Fig. 1 Ag NPs synthesized using raw cotton fiber. (a) TEM micrograph of Ag NPs. The scale bar is 100 nm. (b) Histogram of particle sizes of Ag NPs fitted to a Gaussian distribution. The average diameter was 10.2 nm. (c) UV/Vis spectra of aqueous Ag colloidal solutions with incremental concentrations (0.01-1 mg/L). The SPR absorption peak for Ag NPs was observed at 417 nm.

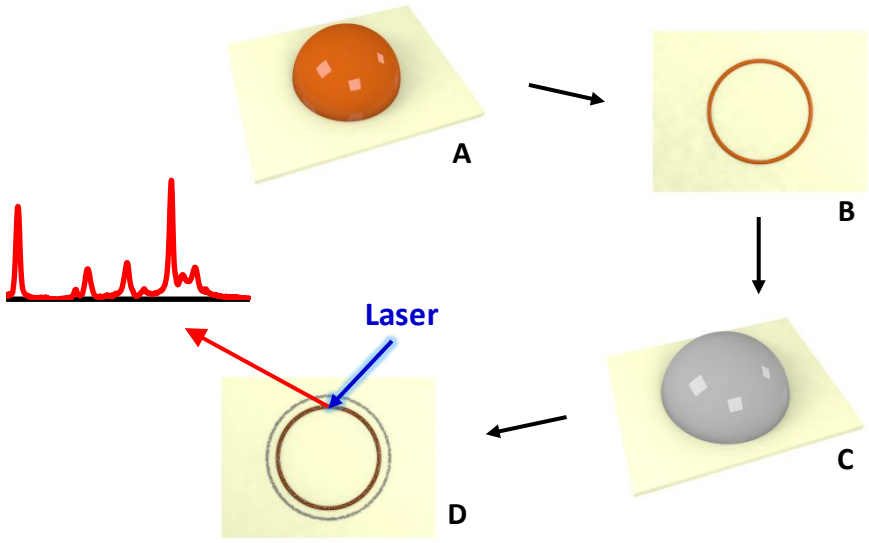

Fig. 2 Schematic of the proposed SERS method: (a) spotting a drop of Ag NP solution, (b) formation of a coffee ring of Ag NPs, (c) spotting a bigger drop of ferbam solution to conjugate with Ag NPs on the coffee ring, and (d) detection of the Ag NP-ferbam complex on the inner coffee ring.

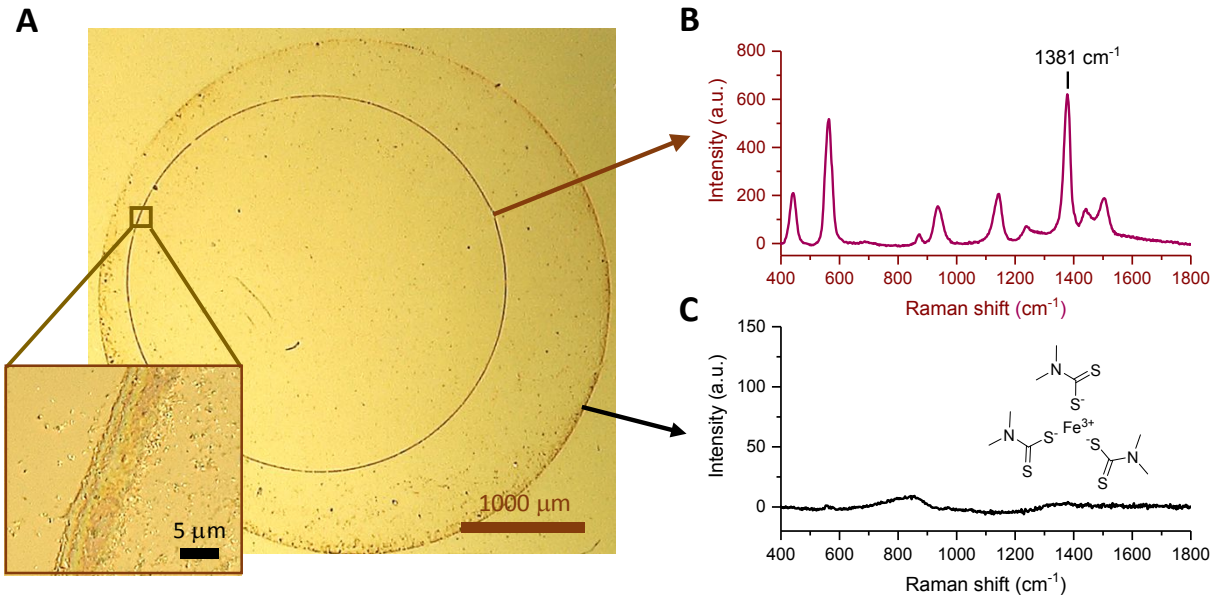

Fig. 3 Conjugation of ferbam onto the coffee ring of Ag NPs in DI water. (a) Optical micrograph of the double coffee ring formed by the method shown in Fig. 2. The concentration of Ag colloidal solution before centrifugation is 0.05 mg/L. The inset shows a close-up of the coffee ring of Ag NPs. The scale bar is 5 µm. Raman spectra of (b) the inner ring and (c) the outer ring are shown. The highest intensity in the SERS signal was observed at 1381 cm^{-1}. The chemical structure of ferbam is shown in the inset.

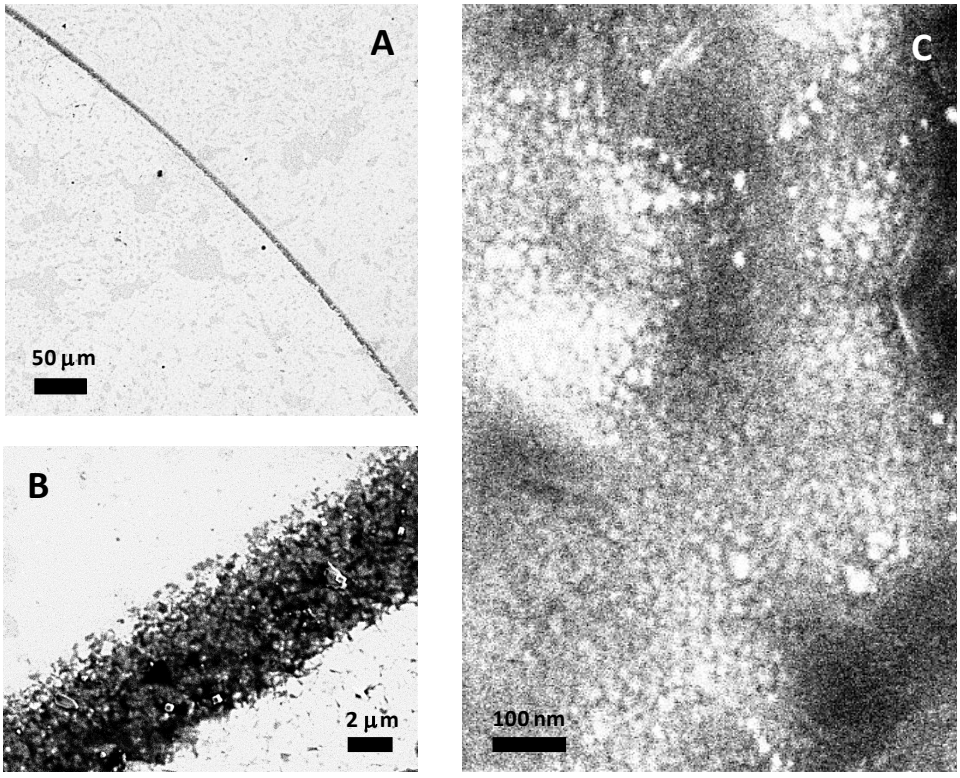

Fig. 4 FE SEM images of the coffee ring of Ag NPs conjugated with ferbam taken at magnifications of (a) ×200, (b) ×5,000, and (c) ×50,000.

Although the employment of noble metallic NPs makes it possible to enhance the Raman signals of target molecules, the resulting signals were poorly reproducible.[38-40] Here, we examined the sensitivity and reproducibility of SERS signals using the proposed method. Figs. 5a and 5b show the SERS spectra obtained from fifty randomly selected locations using this method and the previously published method using the direct conjugation in a solution containing Ag NPs and ferbam,[19] respectively. In the published method, therefore, ferbam was conjugated with individual Ag NPs prior to deposition. It can be seen that the SERS signals for most measurements obtained using this method were greater than those obtained using the published method, demonstrating the superiority of the coffee ring of Ag NPs in the electromagnetic enhancement. The resulting sensitivity was attributed to active SERS sites (i.e., "hot spots") that are located in the junctions between NPs.[27-29] The electromagnetic field in the junction is

intensified, being much greater than the sum of the fields from the individual particles owing to the combined interacting polarization.[28] It was reported that the Raman-enhancement factor in the junction of two Ag NPs (60 nm in diameter) increased from 10^4 to 10^9 when the particle gap was reduced from 9 to 1 nm.[28] As illustrated in the insets, the hot spot (red color) made the aggregated Ag NPs on the coffee ring more SERS-active than individual Ag NPs. Moreover, as the aggregation of NPs was controlled by evaporation kinetics, the resulting spatial orientation contributed to the improved consistency of the SERS signals.

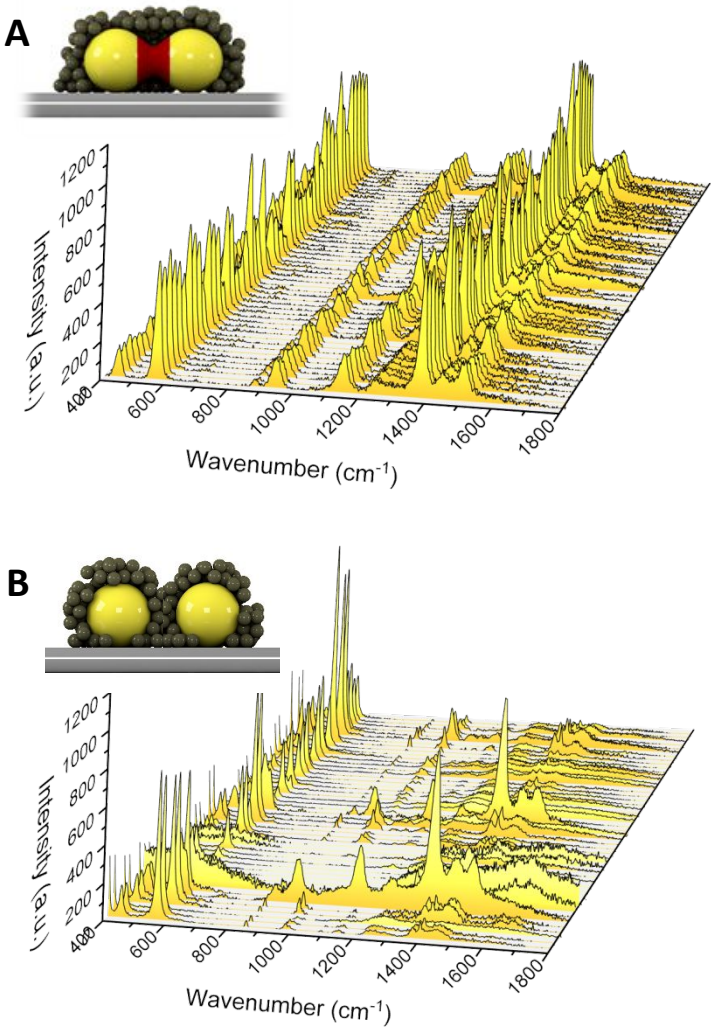

Fig. 5 Sensitivity and reproducibility of SERS signals with 0.1 mg/L of Ag NPs in DI water. (a) SERS spectra collected on the 50 randomly selected spots along the coffee ring of Ag NPs and (b) SERS spectra

obtained using the published method.[19] The inset shows a schematic of a "hot spot" (red) in the junction between aggregated NPs on the coffee ring, which contributed to the sensitivity and reproducibility of the SERS response. Yellow and black indicate Ag NPs and ferbam, respectively.

To examine the suitability of the proposed method for Ag NP quantification, the concentration-dependent SERS response was examined. Figs. 6a and 6b show the SERS spectra (common and full scales, respectively) of ferbam conjugated onto the coffee ring of Ag NPs with incremental concentrations of Ag NPs. As expected, SERS intensity increased as the concentration of Ag NPs increased because of the increased number of active SERS sites occupied by ferbam. This method produced SERS signals at concentrations of Ag NPs as low as 0.01 mg/L (before centrifuge), which was 10 times smaller than that produced by the published method. The spectrum of the lowest concentration, 0.01 mg/L, clearly differed from that of ferbam alone (Fig. 3b bottom). The broad and weak peak at 1381 cm^{-1} of ferbam alone became distinct and sharp with increased intensity upon conjugation with a trace amount of Ag NPs. Such sensitivity was attributed to the magnified electromagnetic field of the particle assembly along the coffee ring. Fig. 7 shows the plot of the intensity at 1381 cm^{-1} as a function of the concentration of Ag NPs. The data points were excellently fitted to a linear relationship, with $R^2 = 0.995$.

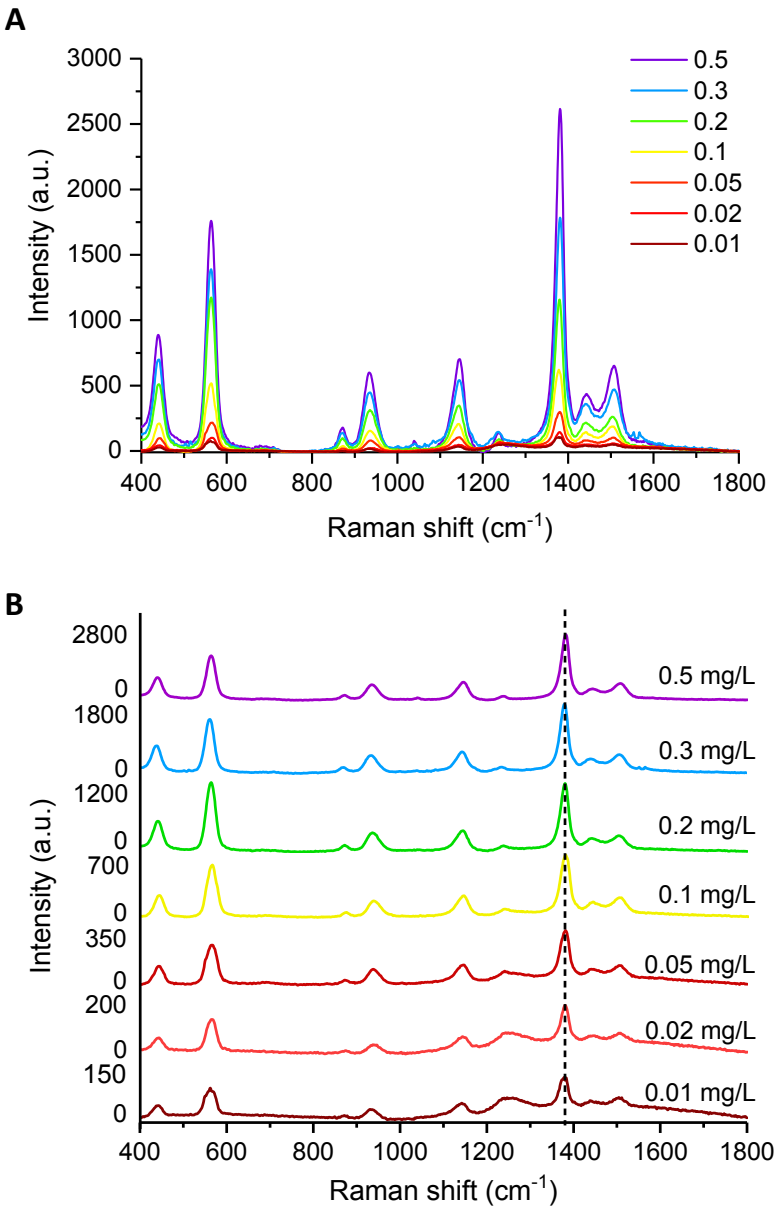

Fig. 6 SERS spectra of ferbam conjugated onto a coffee ring of Ag NPs in DI water with their incremental concentrations. (a) Common scale. (b) Full scale.

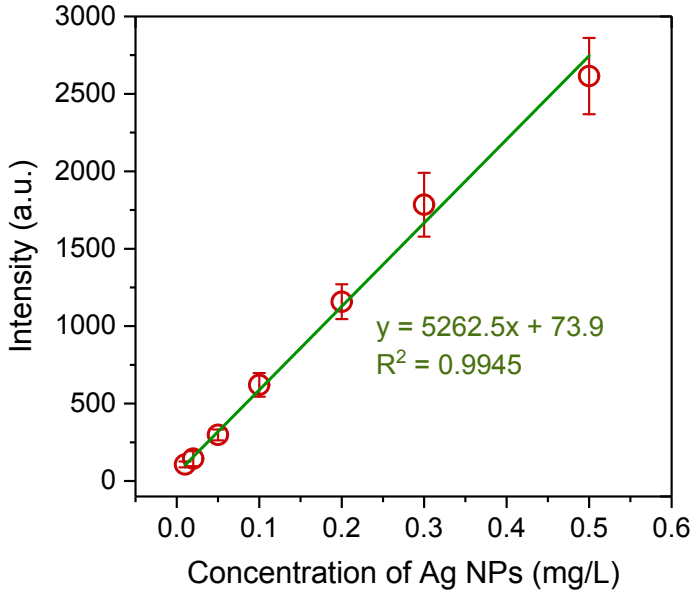

Fig. 7 SERS intensity of ferbam conjugated onto a coffee ring of Ag NPs in DI water at 1381 cm^{-1} as a function of the concentration of Ag NPs. The solid line fits a linear function. The error bars represent the standard errors of 20 measurements.

To apply the SERS method in the analysis of washing solutions, the effects of detergent on the SERS analysis were examined. We chose a commonly used commercial laundry detergent, Tide®, at a concentration of 0.15% w/v. Owing to the reduced surface tension caused by surfactants in the detergent, the droplet of the detergent solution spread farther than the droplet of DI water of equivalent volume. Figs. 8a and 8b compare the evolution of the droplet contact angle and diameter between the detergent solution and DI water, respectively. For the instrumental setting, 1 μL of droplet was used. The immediate contact angle for the detergent solution was almost half that of DI water, i.e. 48° vs. 87°, and the corresponding droplet diameter is 30% larger for the detergent solution. However, their evolution patterns are similar. The contact angle continuously decreased over time. The droplet diameter remained steady until the final three minutes before being completely dried and then decreased. Because of the larger surface area, the droplet of the detergent solution dried more rapidly. The Raman spectrum of ferbam in the detergent solution (Fig. 8c bottom) is almost the same as that of ferbam in DI water (Fig. 3c), showing no SERS

activity in the detergent on ferbam at the concentration used. The Ag NPs dispersed in the detergent solution were SERS-active by the proposed method, developing the enhanced Raman signal of ferbam at the highest intensity at 1381 cm^{-1} (Fig. 3c top). However, its SERS intensity was much lower than the intensity obtained from the same concentration of Ag NPs in DI water. This great reduction is understandable considering the effects of the detergent. The density of Ag NPs must be decreased on a larger coffee ring of the detergent solution droplet. The detergent can also dilute the number of Ag NPs on the ring *via* radial Marangoni flows.[42] More importantly, the complexation of Ag NPs with detergent components such as chloride ions and surfactants will cause the loss of the SERS activity. Despite the reduced intensities, the dependence of SERS response on the concentration of Ag NPs was resolved, producing a linear relationship with $R^2 = 0.991$. To estimate the amount of pure Ag NPs (i.e., Ag NPs not complexed with detergent components) in a washing detergent solution, a calibration curve was constructed with DI water, whose coffee-ring circumference size was matched with that of the detergent solution (4 μL) by increasing the droplet volume (8 μL). Fig. 8d shows the SERS intensities as a function of the amount of Ag NPs in the droplet obtained using 4 μL of DI water (SERS1), 8 μL of DI water (SERS2), and 4 μL of detergent solution (SERS3). The SERS1 is equivalent with the calibration curve present in Fig. 7.

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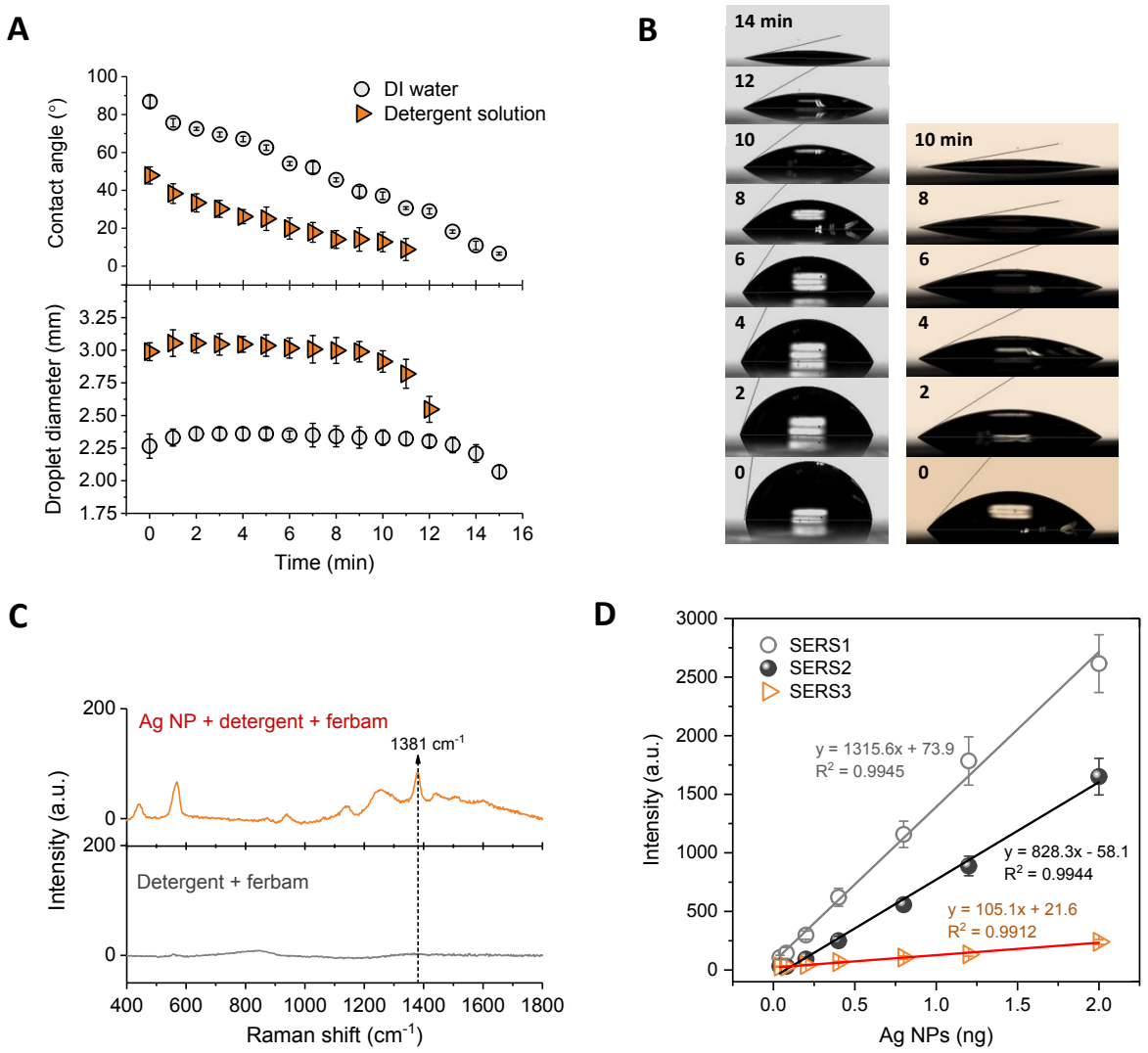

Fig. 8 (a) Contact angles (top) and diameters (bottom) of DI water and detergent solution droplets as a function of drying time. (b) Time-lapse photographs of the spreading of DI water (left) and a detergent solution (right) droplets. (c) Raman spectra of the mixture of detergent (0.15% w/v) and ferbam with (top) and without (bottom) Ag NPs. (d) Calibration curves of SERS intensity as a function of the amount of Ag NPs in the droplet obtained using 4 μL of DI water (SERS1), 8 μL of DI water (SERS2), and 4 μL of detergent solution (SERS3).

The proposed method was applied for assessing the washing durability of Ag NP-treated cotton fabrics. Using the obtained calibration curves (Figs. 7 and 8d), the amounts of Ag NPs detached from the Ag NP-treated cotton fabrics into washing solutions during consecutive launderings were determined.

Figs. 9a and 9b show the concentrations of Ag NPs in washing DI water and detergent solution using the SERS method, respectively, which are compared with those obtained using ICP-MS. In DI water, the concentration of Ag NPs under both methods as the number of laundering cycles increased to 10 laundering cycles and remained steady through further cycles for up to 50 cycles. The concentrations determined using the calibration curve of SERS1 agreed with those determined using ICP-MS, signifying the validity of the SERS method. For washing detergent solutions, two calibration curves—SERS2 and SERS3—were used. The concentrations determined by SERS2 were much lower than the concentrations determined by ICP-MS. Only about 15% of the Ag NPs measured by ICP-MS was detected by the SERS method. This result indicates that a majority of Ag NPs existed as complexation with detergent components such as chloride ions and surfactants. It has been reported that nano- or micron-sized Ti/Si-AgCl, AgCl, and Ag_2S materials existed in laundry detergent solutions after washing textiles containing Ag NPs.[12, 14] On the other hand, the concentrations determined using SERS3, which included Ag NPs that complexed with detergent components, were close to the concentrations determined by ICP-MS. It can be seen that the detachment of Ag NPs from the fabric more readily occurred in a detergent solution than in water. Most of their detachment occurred during first five washings. The percentages lost based on the total Ag NPs in cotton fabric after 5 laundering cycles were 40% and 84% in DI water and detergent solution, respectively, showing the poor washing durability of the surface-treated Ag NPs by a pad-dry procedure.

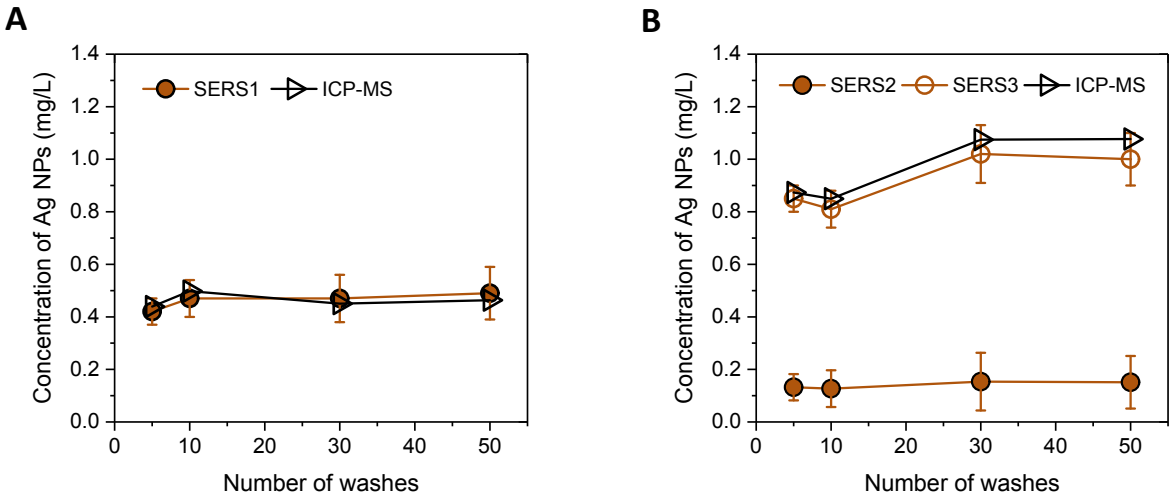

Fig. 9 Concentrations of Ag NPs in (a) DI water and (b) detergent solution after consecutive launderings of Ag NP-treated cotton fabrics determined using the SERS method and ICP-MS. SERS1, SERS2, and SERS3 indicate the data obtained from the calibration curves (Fig. 8d) using 4 μL of DI water, 8 μL of DI water, and 4 μL of a detergent solution, respectively.

4. CONCLUSIONS

In this study, we reported a simple yet effective SERS method for identifying and quantifying Ag NPs in washing solutions to assess the washing durability of textile products containing Ag NPs. The particle assembly formed by the "coffee ring" effect exhibited remarkable surface-enhancement ability in the Raman signal of the indicator ferbam molecule. The sensitivity and reproducibility of the resulting SERS response were greater than those obtained from the complexation of ferbam with individual Ag NPs. This enhancement was attributed to the active SERS "hot spots" located in the junction between aggregated NPs on the coffee ring. The SERS intensities from the coffee rings formed by Ag NPs exhibited linear relationships with the concentration of Ag NPs with $R^2 > 0.99$. Using these calibration curves, the amounts of Ag NPs leached from Ag NP-treated cotton fabrics into washing solutions were quantified. Besides the quantification, which agreed with that by ICP-MS, the SERS method was able to differentiate Ag NPs from other Ag speciation formed in the washing detergent solution. As demonstrated in this study, surface-treated Ag NPs are easily detached from the textiles during washing. The proposed

method is expected to make fast and reliable assessment of the washing durability possible to facilitate the production of safe and leach-resistant Ag NP-functionalized textile products.

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Conflicts of interest

There are no conflicts of interest to declare.

Notes

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