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Multifunctional, flexible and free-standing SERS-active AgNW filter foils

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ABSTRACT

In this work, we report the feasibility of the silver nanowire (AgNW) foils as highly-sensitive, reproducible and facile detection tools for surface-enhanced Raman spectroscopy (SERS) applications. These flexible and free-standing AgNW foils, fabricated by vacuum filtration method following a modified polyol synthesis of AgNWs, are adequately structured for both biological specimen filtering and trace amount of molecule detection simultaneously. The compatibility of AgNW foil in SERS is investigated by using a Raman active molecule of different steric volumes across the filter cross-section. We have shown that AgNW foils exhibit extremely strong SERS activity with detection limit up to 10^{-9} M of crystal violet (CV) molecule with 20% variation over $\sim\text{cm}^2$, revealing reliable homogeneity of the acquired signal. While naturally occurring polyvinylpyrrolidone (PVP) layer during polyol synthesis contribute to controlled aggregation, oxidation prevention, and size - shape control purposes, it also creates a major challenge for obtaining enormous enhancement factors. However, controlled thickness of aluminum oxide (Al_2O_3) coating on PVP@AgNW foils affords to achieve higher enhancement factors than the uncoated ones. What is interesting is that the maximum intensity is achieved from two cycles of Al_2O_3 deposited on AgNW foils. This is attributed to the two different origins: first, a higher adsorption affinity of CV molecules to Al_2O_3 layer than PVP layer; second, tunneling barrier formation against quantum tunneling effects.

Keywords: surface-enhanced Raman spectroscopy, plasmon, silver nanowire filter foil, polyol synthesis.

1. INTRODUCTION

Detecting trace amounts of molecules using reproducible surface-enhanced Raman spectroscopy (SERS) active substrates is in great demand as spatial homogeneity opens new possibilities for sensitive measurements to be made more effectively.¹ While SERS avoids the photodecomposition^{2,3} and the necessity of labeling⁴, it serves as an exciting scientific phenomenon providing structural information and ultrasensitive sensing.⁵ Electromagnetic enhancement is the major contribution to the amplification of Raman signals by excitation of plasmon resonances localized within a few nanometers of the metallic nanostructures.⁶

SERS-active substrates are generally made of electrochemically roughened⁷ and spontaneously aggregated colloidal metal nanostructures⁸ leading to a lack of reproducibility and stability. Although the lithographic technique has high sensitivity and reproducibility, it is expensive, time-consuming and requires elaborate preparation methods. Besides having several benefits, it is difficult to achieve size and shape uniformity by the soft template-directed method and template removal after synthesis is necessary for the hard template-directed method. In chemical synthesis, chemical reducing agents are typically used to reduce the dissolved silver (Ag^+) ions to Ag atoms, while polymers and surfactants are used to stabilize the nanostructures during and after formation.^{8,9} However, the polyol process reveals robust and versatile Ag nanostructures with the advantages of low-cost and simplicity of the synthesis.¹⁰ By this method, large

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quantity of end product is acquired for fabrication of the silver nanowire (AgNW) foils to be used as both free-standing surface enhancers and flexible biological specimen filters. AgNW foils are fabricated by vacuum filtration method following modified polyol synthesis for the larger-scale synthesis of AgNWs. Figure 1 shows the SERS activity of the AgNW foils. The detection limit of the AgNW foils is determined to be as low as 10^{-9} M for crystal violet (CV). In this study, we show that higher enhancement efficiency can be acquired by depositing controlled thickness of aluminum oxide (Al_2O_3) on AgNW foils besides promising characteristic for the high thermal stability of these surface enhancers.

Figure 1. SERS intensity spectra of 10^{-9} , 10^{-10} , 10^{-11} M CV on AgNW foils representing average of the intensities obtained at different locations of the substrates.

2. METHODOLOGY

2.1 Dye molecules

CV (*Methanaminium,N-[4-[bis[4-(di-methylamino)phenyl]methylene]-2,5-cyclohexadien-1-ylidene]-N-methyl-, chloride (1:1)*) dye molecules¹¹ are utilized as reporters in SERS experiments. The concentrations required for SERS analysis is acquired by dissolving the proper amount of dye in distilled water. The molecular composition of CV is $\text{C}_{25}\text{H}_{30}\text{ClN}_3$.

2.2 Synthesis of AgNWs

The classical polyol process¹² is modified for larger-scale synthesis of AgNWs. A typical experiment starts with the preparation of an 80 ml and 0.45 M EG ethylene glycol (EG) solution of PVP (monomer-based calculation MW= 55000) and 10 mg sodium chloride (NaCl) (99.5%) in an erlenmayer bulb. Ingredients are dissolved in EG at 100°C , then the solution is cooled down to room temperature. In the meantime, a 0.12 M silver nitrate (AgNO_3) (99.5%) solution in 40 ml EG is prepared at room temperature. After that, the solution is heated at 120°C in a silicon oil bath on a hot-plate. Also, a reflux is used to eliminate concentration changes due to heating. Then, the PVP/EG solution is added into AgNO_3 /EG solution within 10 minutes. The temperature of the oil bath is set to 160°C . When the oil bath reaches the desired temperature, the solution is annealed 90 minutes additionally. Moreover, the solution is stirred at a rate of 1000 rpm through a magnetic stirrer during the whole process. The purification of AgNWs is done by the centrifuge process. To separate PVP and EG from the AgNWs, the solution is diluted with acetone (in a ratio of 1:5) and centrifuged two times at 8000 rpm for 20 minutes. After that, the nanowires are dispersed in ethanol and again centrifuged at 8000 rpm for 20 minutes. The final product is dispersed in deionized water for the AgNW foil fabrication.

2.3 Fabrication of AgNW foils

AgNWs based foils are fabricated by vacuum filtration of the measured amount of colloidal AgNWs through teflon based hydrophilic 47 mm filter papers with $3\ \mu\text{m}$ pore size. Following peeling from the filter, a 40 mm width AgNW based foils are obtained.

2.4 SERS measurements

The SERS signals were collected by f/9.8, 750 mm spectrometer (Andor SR750) with 150 l/mm grating. The measurements were done by the Andor Newton EMCCD camera. The Raman excitation from a DPSS Nd-YAG laser operating at 532 nm of wavelength was delivered through a 100 μm diameter core visible multimode optical fiber with a collimator in conjunction with a non-polarizing 50/50 beam splitter cube. A Nikon Eclipse LV100 microscope equipped with a 100XA/0.90 NA Nikon objective was used to focus the laser light onto the sample surface. Another 100 μm diameter core multimode visible optical fiber with a collimator attached to the other port of the beam splitter cube was used to deliver the collected Raman signal from the microscope to the spectrometer.

3. RESULTS AND DISCUSSION

AgNW foils are fabricated by vacuum filtration method as shown in Figure 2 (b) following colloidal AgNWs synthesis through polyol synthesis. In polyol synthesis, EG is used as both solvent and reducing agent, PVP is used as a stabilizing agent, AgNO_3 is used as Ag source and NaCl is used as an inhibitor as shown in Figure 2 (a). Figure 2 (c) and (d) show photograph of AgNW foil with 40 mm width and scanning electron microscopy (SEM) image of AgNW foils in higher magnification with 5 μm scale bar, respectively. The SEM image highlights that the foils do not have packed structure instead they have porous-like structure. Besides, Figure 2 (e) shows the cross-sectional SEM image of AgNW foils with approximately 80 μm of thickness.

Figure 2. a) Main objectives of the ingredients for the synthesis of AgNWs, b) image of the experimental setup of vacuum filtration method, c) photograph of the AgNW foils, d) top-view, and e) cross-sectional SEM images of AgNWs foils.

3.1 SERS measurements

CV molecule is used as the analyte molecule to characterize the SERS activity and signal homogeneity of the AgNWs foils. Firstly, 10^{-5} M CV is deposited by drop-casting on a 1 cm^2 large AgNW foil surface and SERS measurements are recorded from 5 different locations of the prepared sample surface with 20% variation in the signal as shown in Figure 3. All vibrational modes of the CV molecule could be observed for 10^{-5} M.

The corresponding SERS spectrum reveals CV modes at 811 cm^{-1} and 1178 cm^{-1} (the C–H bending vibrations), 915 cm^{-1} (the radical-ring skeletal vibration), 1361 cm^{-1} (the C–C_{center} stretching vibration), 1587 and 1616 cm^{-1} (the C–C stretching vibration of the phenyl ring).¹³ Then, further measurements were also made with lower molarities of CV molecule to determine the detection limit of the AgNW foils to be used as SERS substrates. All vibrational modes of 10^{-5} M to 10^{-9} M CV solutions could be observed. SERS measurements for 10^{-10} and 10^{-11} M CV molecules reveal three strong peaks at 1612 , 1766 and 2946 cm^{-1} which belong to the PVP polymer. These preliminary studies indicate that polyol synthesized foils offer to be used as effective signal enhancer substrates.

Figure 3. SERS intensity spectra of 10^{-5} M CV on AgNW foil obtained at 5 different locations of the substrate.

3.2 SERS studies with controlled distance between antennas and molecules

The enhancement mechanism is investigated through depositing controlled thickness of Al_2O_3 on free-standing AgNW foils by atomic layer deposition (ALD). ALD method offers exceptional conformality on high-aspect-ratio structures, thickness control at the Angstrom level, and tunable film composition.^{14,15,16} Hence, Al_2O_3 was deposited at different thicknesses by ALD onto AgNW foils. It is important to detect CV molecule sensitively because this molecule can easily enter into negatively charged cells membrane and concentrate in the cytoplasm.¹⁷ To investigate the SERS activity, CV molecules were adsorbed on these plasmonic nanostructures. Figure 4 (a) shows intensity spectra of 10^{-4} M CV at 5 different locations of AgNW foil with signal homogeneity of 15%. Figure 4 (b) shows mean intensity spectra of 10^{-4} M

Figure 4. (a) Intensity spectra of 10^{-4} M CV from 5 different locations of AgNW foil, (b) mean intensity spectra of 10^{-4} M CV from 2, 5, 10 and 15 cycles of Al_2O_3 deposited on AgNW foils, (c) box charts displaying the statistics of SERS measurements of 10^{-4} M CV molecule on bare and ALD deposited AgNW foils and (d) mean integrated intensity values of these statistics.

CV from 2, 5, 10 and 15 cycles of Al₂O₃ deposited on AgNW foils. Statistics of these measurements are presented in Figure 4 (c) with the spectrum obtained from the CV molecule on bare AgNW foil in addition to the different cycles of Al₂O₃ deposition. Figure 4 (d) shows mean integrated intensity values acquired from integrated intensity range statistics with Al₂O₃ thicknesses for the corresponding number of cycles.

SERS enhancement arises from the strong localization of the near field close to the metal nanostructures and it decays rapidly further away from the particle surface.¹⁸ In fact, when increased surface area scaling with r^2 is considered, r^{-10} distance dependence is observed for the electromagnetic enhancement of SERS, where r is the distance from the surface to the analyte molecule.¹⁹ According to our results, the signal intensity decreases as the number of cycles increases as predicted. What is interesting is that the maximum intensity is obtained for two cycles of Al₂O₃ coating on PVP@AgNW foils when compared to the uncoated one. The CV molecule is a cationic dye that can easily interact with negatively charged surfaces.¹⁷ Because the Al₂O₃ films contain fixed negative charges^{20,21} adsorption affinity of CV molecules on the Al₂O₃ layer is higher as compared to the PVP layer which is non-charged polymer.²² However, after 2 cycles of Al₂O₃ deposition, electromagnetic field effect overcomes the number of adsorbed molecules and mean integrated intensity decreases with further Al₂O₃ deposition. Zhang et al investigated the SERS activity of calcium dipicolinate (CaDPA) on Al₂O₃-modified Ag film-over-nanosphere substrates fabricated using ALD. They stated that two ALD cycles of Al₂O₃ optimize the detection due to the greater binding affinity of CaDPA toward Al₂O₃ compared to Ag.²³ In addition, quantum mechanical effects such as quantum tunneling is known to alter Raman intensity adversely.²⁴ A second effect behind this observed increase in SERS for two cycles of ALD deposition might be due to forming a tunneling barrier against quantum tunneling effects. Al₂O₃ layers over Ag nanostructures preserve SERS efficiency at high temperatures due to the controllable pinhole rate by tri-methylaluminum (TMA) exposure time during ALD coating.²⁵ Ma et al showed that the melting point of Ag nanorods increases monotonously with the decrease of pinhole rate, starting from 257°C with ~18.0% pinholes and reaching a maximum at 277°C when the pinhole rate was ~5.3% by 2 ms and 100 ms TMA exposure time, respectively. We have deposited Al₂O₃ with 30 ms TMA exposure time such that pinhole rate of the end products that are used in our experiments are highly promising for preserving SERS efficiency at temperatures higher than 250°C with strengthened thermal stability.

4. CONCLUSIONS

We state that higher enhancement factors are achievable by deposition of Al₂O₃ on AgNW foils with the advantage of high-temperature SERS sensing ability although the presence of the PVP layer. Various SERS substrates are commercially available; however, SERS addresses the detection of single molecules, and existing approaches are not effective on larger objects such as nano- and micro-particle contaminants. The fabricated foils do not have a packed structure, instead, they have a porous-like structure. Therefore, AgNW foil can perform two different tasks: contaminant filtering and Raman enhancement.

As shown in Figure 1 and Figure 3, there are backgrounds toward higher wavenumbers and 10⁻⁹ M is the limit of detection of the chosen Raman active molecule, because these filter foils contain PVP layer around them. Hence, removal of the PVP layer around the AgNW foils is a mandatory task to be able to detect micrometer scale contaminants as requiring improved sensitivity of SERS substrates. To that end and as a future work, the Raman activity of the PVP free AgNW foils will be investigated by using different molecules of different steric volumes across the filter cross-section. Besides, SERS EF values will be calculated for designed experimental conditions to demonstrate the activity and sensitivity of the PVP free filter foils for micro-particle contaminant filtering and detection.

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