

Silver Dendrites from Galvanic Displacement on Commercial Aluminum Foil As an Effective SERS Substrate

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Silver is used in a wide range of applications, including photography,¹ catalysis,² optics,³ bactericidal coatings,⁴ microelectronics,⁵ and sensing.⁶ In the latter case, it is found to be the most effective material for surface enhanced Raman spectroscopy (SERS), a phenomenon first reported in 1974 by Fleischman et al.⁷ Many varied silver structures and substrates have been reported as effective enhancers of the weak basic Raman signal, with the use of nanotechnological approaches being the latest trend in this field.^{8–12}

Here we present a cost-effective and simple method, based on a wet chemical fabrication approach, to produce SERS substrates in a reliable way. Our method involves the galvanic displacement (also known as electroless deposition) of silver on commercial aluminum foil. It is subsequently demonstrated that the thus-obtained silver structures can be removed from the Al foil and be redeposited on any desired substrate. Previous works by Brevnov et al.¹³ reported galvanic displacement on aluminum foil containing copper but were unable to reproduce the process on pure aluminum because of the presence of superficial aluminum oxide layer. Zuo and Jagodzinski proposed a method for the deposition of silver on aluminum foil and its use to study pyridine adsorption via SERS by employing extremely high concentrations of silver dissolutions, making the process costly for large-area substrate fabrication and constrained to Al.¹⁴

Our process reported here, which involves the removal of the native aluminum oxide layer, succeeds in the galvanic exchange of Al and Ag, producing a large amount of silver microdendrites that present high potential as SERS-active substrates. The formation of silver dendrites via galvanic deposition has been reported using silicon¹⁵ and copper¹⁶ as substrates. However, these approaches suffer from the inconvenience of weak adhesion between the dendrites and the substrates as well as the poor control over the formation of dendrites, which hinders the ability to control the “hot-spot” locations. The use of silicon or copper as part of the production process is also confining. In our case, the thus-obtained dendrites form a silver paste that can be subsequently spread in a simple manner on any desired surface, including its use as ink for massive screen printing production. This feature provides extreme versatility, including cost effectiveness, in the final design of SERS-active substrates. The process also opens up opportunities with regard to chemical sensing on flexible substrates.

AgF (99.9%) A.C.S. grade (Sigma-Aldrich Co. Ltd.) was used for the preparation of the 20 mM galvanic displacement plating solution. The chemicals 1,2-benzenedithiol, 1-phenylethyl mercaptan, and 2,2'-dithiopyridine (all from Sigma-Aldrich) were used as SERS analytes by preparing 100 μ M stock solutions in methanol (EMB) to produce self-assembled monolayers (SAM) of these

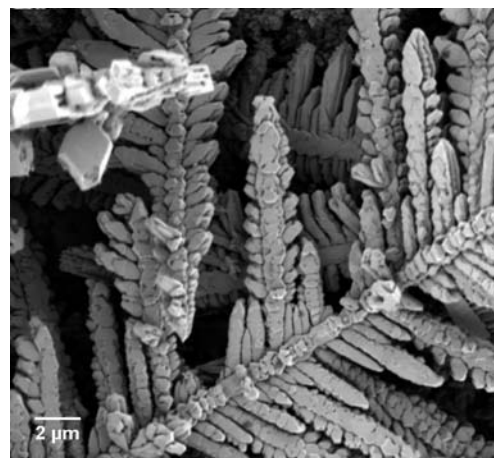


Figure 1. SEM image of silver dendrites formed on Al foil.

species. These analytes were chosen as they present similarities in their molecular structures (namely, aromatic rings and thiol groups in all cases), but they also present subtle variations such as the nitrogen heteroatom in the pyridine ring or the binding nature of the thiol groups to the surface. Because of the presence of aromatic rings, strong Raman bands are expected at $\sim 1000\text{ cm}^{-1}$ where the ring breathing modes appear and at $\sim 1600\text{ cm}^{-1}$, for ring deformation modes in all cases, and these peaks served as Raman labels.

Commercial aluminum paper was cut into $2 \times 2\text{ cm}^2$ foils and rinsed with acetone and water for degreasing. Immersion in concentrated HF was carried out for 10 s to etch the native aluminum oxide layer. After rinsing in water and drying in N_2 , the aluminum foils were immediately immersed in the 20 mM AgF solution for 24 h in the dark to avoid silver photoreduction. A large amount of silver dendrites were formed all over the aluminum foil. Dendrites were detached from the aluminum foil by rinsing in water and then filtered and dried in air, resulting in a dense Ag paste. Silver dendrites were subsequently spread on double-sided Scotch tape previously attached to a paper that served as a microscope slide. This forms the substrate used for the SERS analysis that is described in the text. Standard materials and chemical processes were used to demonstrate the promise and simplicity of the presented SERS application. Silver dendrite excess was removed by blowing a gentle flow of N_2 .

Figure 1 shows a scanning electron microscopy (SEM) image of the formed dendrites. The large area-to-volume ratio suggests these dendrites as promising SERS substrates, as they also present a high concentration of edges and terraces, features that are believed to provide higher signals. X-ray photoelectron spectroscopy measurements revealed the Ag(0) nature of the formed structures. The reaction yield was found to be $\sim 40\%$ in terms of dry Ag(0) dendrite

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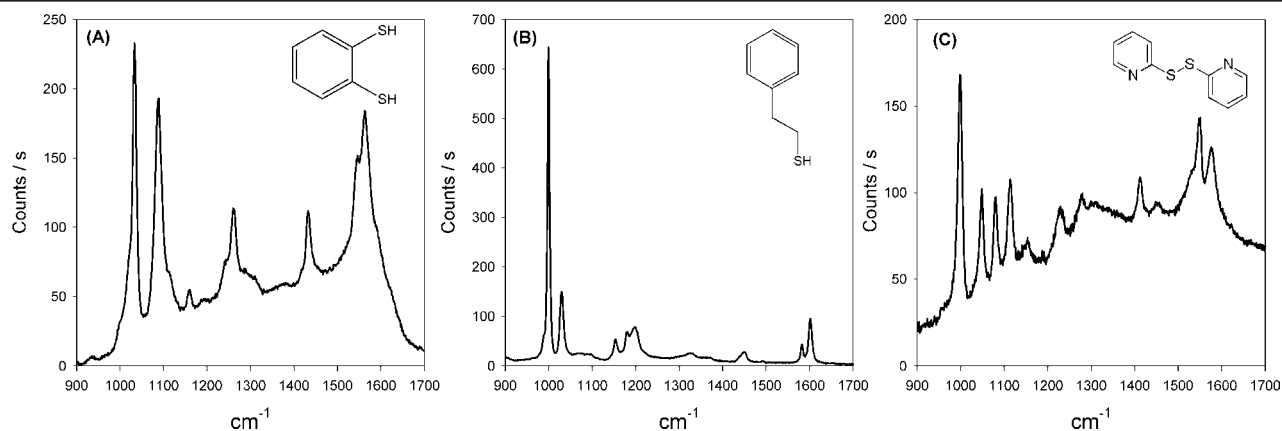


Figure 2. Raman spectra of the formed SAMs on Ag dendrites for the three different analytes: (A) 1,2-benzenedithiol, (B) 1-phenylethyl mercaptan, and (C) 2,2'-dithiodipyridine. Laser excitation wavelength of 632.8 nm.

weight after filtration and drying. Even with this nonoptimized yield, the process promises to enable the mass production of low-cost SERS substrates

For SERS measurements, the substrates were incubated for 24 h in a 100 μM standard of the different analytes. Raman measurements were performed after rinsing and sonication to ensure that only a monolayer is present in the substrate. Figure 2 shows the Raman spectra obtained on the three aforementioned SAMs. Each Raman spectrum was the result of averaging 10 scans with a 10 s integration time in the 920–1700 cm^{-1} region. SERS hot spots are considered to be the dendrite branches and thus localized by optical focusing on the surface.

As can be observed in Figure 2, excellent Raman spectra were obtained in all three cases, presenting good band resolution and a high Raman signal. Taking into account that the presented spectra correspond to monolayers of the used analytes, high Raman enhancements can be expected. The differences in peak height at approximately 1000 and 1600 cm^{-1} can be attributed to the variations in monolayer packing and ordering. Previous work by Hu et al. attributed the differences in Raman peak intensities in terms of packing density and bonding when investigating the Ag–S interaction using pyridine as the analyte.¹⁷ Similarly in our case, 1-phenylethyl mercaptan presents a single anchoring thiol that permits a well-organized highly packed SAM. On the other hand, 1,2-benzenedithiol can attach by either one or two thiol groups; because of the double bonding configuration, it is likely that the formed SAM presents defects, pinholes and poorer packing in this case. Finally 2,2'-dithiodipyridine can only interact with the silver substrate via π -bonding, forming a monolayer of horizontally oriented molecules that leads to a less densely packed SAM. Because of the different packing configuration and density, 1-phenylethyl mercaptan presents the highest breathing-mode intensity, in accordance to the number of aromatic rings involved in the measurement, but also presents the lowest ring deformation peak, possibly because of the high packing density of the rings that impedes the deformation due to the presence of neighboring aromatic rings. On the other hand, 1,2-benzenedithiol and 2,2'-dithiodipyridine present lower breathing peaks, but higher deformation peaks, confirming the different nature of the SAM packing in these molecules. Considering the absolute values of the obtained Raman signals, it can be stated that, with the proposed method, it is possible to achieve similar Raman signals when compared to other more complicated and expensive substrates reported previously.¹⁰

In summary, effective and flexible SERS substrates have been developed by using commercial aluminum foil and silver fluoride

as the sources for obtaining silver dendrites that present high surface area-to-volume ratios and are easy to manipulate to fabricate highly effective SERS substrates in a massive way. Three different analytes were tested with excellent Raman results when measuring the Raman spectra of formed SAMs only on the silver surface. The ability to use the dendrites as a paste has provided the ability to spread the dendrites onto any desired surface, including flexible substrates as shown here, and by using methods such as screen printing. The simplicity and cost of the overall process makes this procedure an excellent candidate for analytical SERS control processes or for easy in-the-field measurements.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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