

Improving Patterned Nanoporous Gold as an Effective Surface-Enhanced Raman Scattering Template

James S. Kyne, Gilberto A Rodriguez, and Sharon M. Weiss

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BRIEF. An imprinted nanoporous gold substrate was optimized to create a low power Raman biological and chemical sensor.

ABSTRACT. Surface enhanced Raman spectroscopy (SERS) is a promising sensing technique for identifying and quantifying specific chemical and biological species for applications in food safety, medicine, environmental monitoring, and the military. When light interacts with a material, a small fraction of photons ($\sim 10^{-6}$) are inelastically scattered – Raman scattered – and shifted in wavelength by a magnitude corresponding to specific molecular bonds present in the material. However, detecting this molecular footprint outside of a laboratory is a challenge due to poor inelastic scattering and equipment limitations involving sensitivity and cost. The addition of SERS substrates can mitigate this issue by amplifying the emission of inelastically scattered photons when target molecules are placed within a strong electric field. To date, commercial SERS sensors are limited in their ability to measure uniform, strong Raman scattering using low cost materials. This work optimizes the fabrication of a patterned nanoporous gold (PNPG) SERS substrate that has been shown to amplify Raman scattering by nearly eight orders of magnitude. Two methods to further enhancement were studied: optimizing the imprinting force and adding ~ 90 nm gold nanoparticles to the PNPG. A threefold improvement was demonstrated, making PNPG substrates even more promising for incorporation in field-deployable SERS sensors.

INTRODUCTION.

Chemical and biological sensors can be used as preventive diagnostics tools in many applications, including alert a military troop if they are in the presence of an explosive, detect the presence of harmful pesticides, bacteria, or viruses in food, and detect illnesses that could potentially be fatal [1]. One of the most promising methods of detection is measuring optical interactions with the target analyte of interest; Raman scattering can accurately identify and quantify hazardous materials with limited sample preparation. Raman scattering is a type of photon-molecule interaction in which the photon gains or loses energy from its interaction with the molecule in an inelastic interaction. This change in the photon's energy can be measured in its wavelength

$$E = hc/\lambda$$

where E is energy, h is Planck's constant, c is the speed of light, and λ is the wavelength of light. A molecule will absorb and radiate energy based on its geometrical structure, which translates to every Raman-active molecule having a specific Raman "fingerprint." The intensity of scattered photons at the shifted wavelengths are measured using a Raman microscope. This yields wavelength-resolved spectral data in Raman shift units (typically cm^{-1}).

Currently, field deployable Raman scattering devices are being used for detection of molecules in relatively high concentrations. It is possible to detect single molecules in some cases using Raman scattering, but it requires a high-powered laser ($>5\text{mW}$) and a high sensitivity detector [1]. Increases in Raman intensity can be significantly enhanced when the analyte is placed within the strong electric field of a plasmonic surface [2]. This higher sensitivity is important because a lower concentration of molecules can be accurately detected and expenses on lasers and detectors can be minimized. Placing a target molecule on certain metals such as gold, silver, and aluminum has been shown to improve Raman scattering rates; commercially available samples improve Raman scattering

rates by six orders of magnitude (10^6) [3]. This technique is called surface enhanced Raman spectroscopy (SERS).

Current research is focused on creating SERS substrates that are practical, inexpensive, accurate, and can be fabricated uniformly over large areas ($>\text{cm}^2$). A common SERS surface consists of colloidal gold particles and has "hotspots" or areas that have very good electric field enhancement and give high rates of Raman scattering; however, these areas occur randomly or have very low surface areas [4]. Other SERS samples are made with a uniform pattern that creates a uniform rate of Raman scattering but enhancement is not as high as areas with hotspots, for example a commercially available substrate Klarite® has a uniform enhancement, but the enhancement is only around 10^6 .

PNPG is a promising SERS template that can be incorporated into field sensors to reduce equipment costs and improve on detection sensitivity of hazardous molecules. The primary goal of this project is to improve upon an already effective method of creating a SERS substrate for field devices without increasing the cost of fabrication or reducing the reproducibility of the measured SERS signal across the substrate.

A method of creating a uniform, inexpensive SERS substrate with high electric field enhancement was developed by selectively patterning nanoporous gold with a two-dimensional grating. The grating was designed to maximize the plasmonic effect at the metal surface and to provide a surface roughness that allows hotspot like enhancement [5]. The grating is patterned by a process known as direct imprinting of porous substrates (DIPS), a fast, inexpensive, and straightforward technique that allows patterning or stamping of nanoscale features into porous materials over a large area [6]. DIPS uses a lithographically etched pattern in a reusable silicon master stamp and mechanical pressure to transfer the stamp features into the porous substrate, in this case patterned nanoporous gold (PNPG) [6]. The PNPG SERS substrate has been reported to enhance Raman scattering by nearly eight orders of magnitude, which is higher than that of similar products such as Klarite [7].

MATERIALS AND METHODS.

Sample Preparation.

The A base of 100nm thick nanoporous gold film was applied to a gold-coated silicon chip in all experiments. The silicon chip served as a convenient base for the nanoporous gold film but other supporting substrates such as glass or polymers can be used. The nanoporous gold was fabricated by placing 100nm gold-silver leaf in nitric acid for fifteen minutes at room temperature, a previously established technique [5]. The nitric acid (70% HNO_3) dissolved the silver from the leaf, leaving behind a gold network with porous voids where the silver was removed. This created a uniform roughened texture that helps to enhance Raman scattering. The nanoporous gold then soaked in deionized (DI) water for five minutes to rinse away any remaining nitric acid in the nanoporous gold. Following the rinse, the nanoporous gold was attached to the supporting gold-coated silicon substrate. For this experiment, the gold was chemically modified with 1,6-hexanedithiol to chemically bond the porous film to the supporting Au-Si wafer [8].

Once the sample was created, the nanoporous gold was imprinted with the two-dimensional grating pattern using the DIPS method. DIPS was done by placing a lithographically etched silicon wafer on top of the nanoporous gold and hydraulically adding pressure [6]. Taking a few seconds, this mechanically transferred the pattern from the silicon master onto the nanoporous gold.

To quantify the intensity of Raman scattering signal, each sample was soaked in a 0.2 mM benzenethiol solution in ethanol for 1 hour. Due to the nature of benzenethiol, the natural formation of a self-assembled monolayer ensures all samples and surface areas are uniformly coated. Next, the samples were rinsed with ethanol and dried with nitrogen. Measurements of the Raman shift were taken on a Thermo Scientific DXR™ Raman Microscope with a 780nm laser. Samples were measured with 1 mW laser power, a 50 μm slit aperture, and a 10 \times microscope objective.

Optimizing Imprintation Force.

To find the optimal imprintation force, a 3.6mm x 3.6mm silicon stamp was used for imprintation starting at a pressure of 80 psi. Pressure was increased incrementally by 10 psi until the pattern was fully transferred, then increased in intervals of 5 psi until the stamp or PNPG sample was damaged (170 psi).

The Addition of Gold Nanoparticles.

Gold nanoparticles were the second method attempted to improve Raman scattering. The gold nanoparticles (~90nm diameter) were suspended in DI water, and pipetted onto the PNPG, which dried overnight to leave a uniform layer. The size of the gold nanoparticles was selected to match the absorption wavelength peak of the plasmon excitation wavelength created by the grating on the PNPG; this was expected to give rise to the largest enhancement in Raman scattering intensity.

RESULTS.

Optimal Pressure.

Figure 1 shows the Raman intensity at 1070 cm^{-1} , a known peak on the SERS spectrum of benzenethiol, for various DIPS pressures. A polynomial trend is observed, with a maximum Raman intensity near 130 psi. It should be noted that the psi readings in Chart 1 do not reflect the actual pressure applied to the stamp, but rather the pressure of the hydraulic fluid in the press used to carry out DIPS.

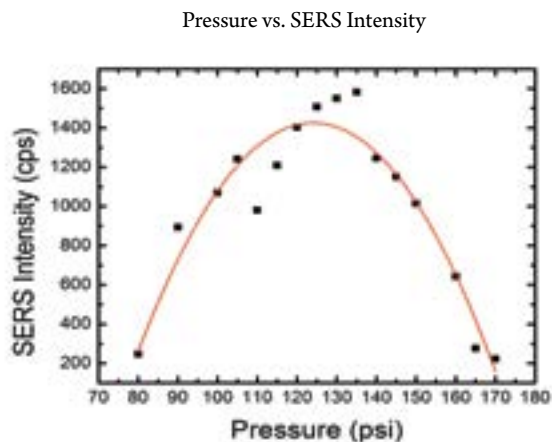


Figure 1. Pressure vs. SERS Intensity. This shows there is a correlation between pressure and SERS intensity.

Gold Nanoparticles.

Figure 2 shows the difference in enhancement of various substrates, including nanoporous gold (NPG), nanoporous gold with gold nanoparticles (NPG + Au), patterned nanoporous gold (PNPG), and patterned nanoporous gold with gold nanoparticles (PNPG + Au). As seen, the addition of gold nanoparticles resulted in a substantial enhancement of the Raman scattering intensity compared to samples measured without the gold nanoparticles. The addition of the ~90nm gold nanoparticles increases the localized surface plasmon intensity, further enhancing the Raman scattering intensity. The gold nanoparticles give a Raman scattering intensity approximately three times what was previously observed from optimal pressure patterned nanoporous gold.

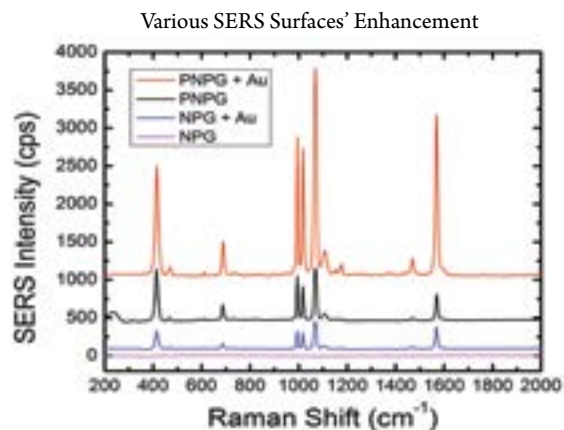


Figure 2. SERS differences due to substrate materials. This shows a typical Raman spectroscopy graph for various substrates. Shown above are nanoporous gold (NPG), nanoporous gold with gold nanoparticles (NPG + Au), patterned nanoporous gold (PNPG), and patterned nanoporous gold with gold nanoparticles (PNPG + Au).

DISCUSSION.

The two methods were successful in improving the SERS enhancement while maintaining repeatability, low-cost, and rapid fabrication of the original PNPG. Finding the optimal pressure of a press can be accomplished easily, and the addition of gold nanoparticles takes approximately thirty seconds. The gold nanoparticles' suspension fluid must evaporate in order for the sample to be functional, but this time can be shortened if carried out at an elevated temperature. The successful methods detailed in this work were found to increase the rate of Raman scattering over threefold.

In terms of pressure, the beginning pressure (80 psi) did not imprint the nanoporous gold uniformly, and the last pressure (170 psi) caused damage to the stamp and porous gold film. However, there was a correlation between pressure and Raman intensity. The enhanced roughness of the nanoporous gold surface after deposition of nanoparticles likely contributed to the increased Raman scattering intensity that was measured.

This work signifies the importance of a pressure optimization step in the DIPS procedure. Variability in stamp size and press systems can be overcome through the pressure optimization procedure presented in this work, making the process transferable to different setups and configurations. It is important to note pressure must be adjusted when working with different stamp sizes.

This work demonstrates that SERS enhanced Raman spectroscopy is a viable option for molecular identification applications requiring high sensitivity and cost effective options.

CONCLUSION.

This work has successfully improved upon nanoporous gold as an effective SERS template. Current affordable field devices have low powered lasers, so in order to detect low concentrations of a molecule, the SERS substrate enhancement must be very high. By using optimal pressure during DIPS patterning and adding gold nanoparticles, an increase of at least threefold in the SERS signal enhancement is observed compared to the SERS signal measured on a previously demonstrated patterned nanoporous gold SERS substrate. PNPG SERS substrates offer potential solution for field-based Raman measurements as they can be fabricated at a fraction of the cost and give much higher Raman scattering intensities due to the special patterning of the samples. This enhanced performance will directly lead to a reduced limit of detection for field-deployable Raman spectrometers.

Previous studies have shown imprinted nanoporous gold to be a low cost, quick and effective template for surface enhanced Raman spectroscopy (SERS) [5]. This work improves upon that template by demonstrating an even higher rate of Raman scattering, while maintaining the low cost and rapid fabrication.

This study is unique in that it improves upon a method for SERS substrate fabrication that is already very novel in its low cost and ease of production. This study creates additional steps to maximize SERS enhancement without increasing costs or complicating the fabrication procedure. The overall goal was to have a low cost yet effective SERS template, which was achieved. The SERS substrate fabrication method created in this research allows for lower cost substrates, as well as higher enhancement than commercially available.

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James Kyne is a senior at Hume-Fogg Academic High School in Nashville, Tennessee; he attended the School for Science and Math at Vanderbilt.