

Integrated Surface-Enhanced Raman Spectroscopy Sensors for Process Monitoring

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ABSTRACT

A scalable and economic approach for fabricating plasmonic nanostructures, a product of fundamental research in nanoscience at the University of Maryland, enables the integration of plasmonic metamaterials in optical windows, capillary tubes and optic fibers. These plasmonic metamaterials are engineered to produce a strong, distinct and reliable response in the presence of chemicals through the surface-enhanced Raman scattering (SERS) method. These sensing elements now offer in-situ, remote and high-throughput Raman sensing of trace-level organics with unprecedented reproducibility.

Keywords: plasmonics, chemical sensing, optic fiber, high-throughput, in-situ

1 INTRODUCTION

Optical metamaterials obtain their unique properties from the combination of nanoscale plasmonic components and dielectric components. Until recently, reproducible mass-production of metamaterials has proven to be challenging. Here, we have employed a patented technology for the manipulation of inorganic nanoparticles that enables us to fabricate functional metamaterials in a variety of forms (plates, tubes, fibers, etc.). These products were utilized as SERS substrates and have demonstrated large enhancement factor values that are consistent over large active areas [1,2]. When incorporated as optical windows or optical fiber probes in a dynamic chemical environment, trace detection of organics with selectivity for particular chemical functionalities is achieved. This technical paper describes the structure of the metamaterial and experiments demonstrating its use as a molecular sensor incorporated in a viewport optical window, a flow-cell capillary, and an optic fiber remote sensing probe.

2 METAMATERIAL STRUCTURE

The metamaterial that generates the SERS signal in response to molecular adsorption has the structure shown schematically in Fig. 1A. On the side exposed to the chemical environment, the metamaterial consists of a periodic two-dimensional array of nanoparticles of controlled diameter. The nanoparticles are made of a

plasmonic metal. Gold nanoparticles are used throughout this paper, chosen for their inertness and stability. The gold nanoparticles adhere to the surface of a block co-polymer film. The block co-polymer film and a multi-layered film structure beneath it control both the assembly of the individual nanoparticles into an ordered array and the plasmonic coupling between the nanoparticles in the array.

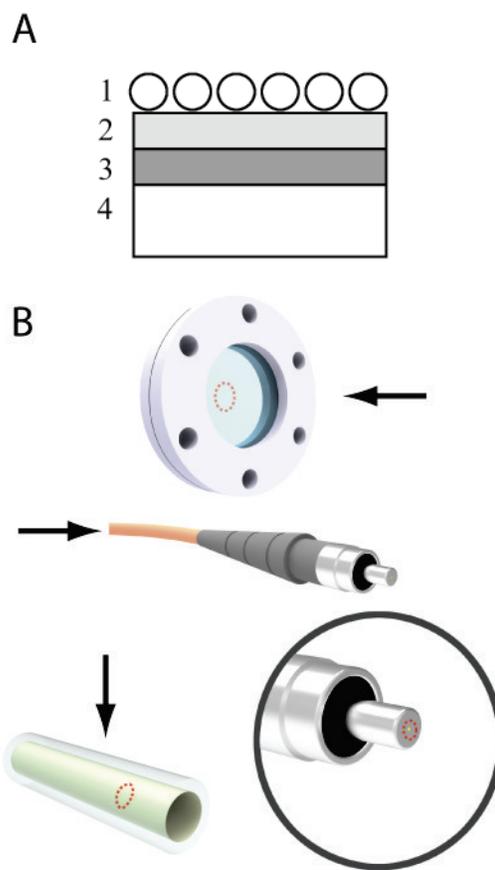


Figure 1: (A) Schematic of the structure of the metamaterial. 1. Nanoparticle array. 2. Block copolymer film. 3. Multilayer film. 4. Support. (B) Diagrams of a viewport, optic fiber and capillary tube, showing the location of the metamaterial (dotted red boundary) and the incoming illumination for Raman spectroscopy (arrow).

The block co-polymer film exhibits nanoscale texturing achieved by self-assembly of its polymeric components. Through coulombic interactions, the block co-polymer film guides the self-assembly of the gold nanoparticles into a surface-adsorbed two-dimensional array of nanoparticles, when it is immersed in an aqueous solution of these nanoparticles. [3] Beneath the block co-polymer layer are dielectric and metallic thin-films that modulate the inter-particle plasmonic interactions. Through the modification of the layered structure and the size of the gold nanoparticles, an optimal metamaterial is engineered and tailored to the specific Raman spectroscopy instrumentation and application of the end-user. [2] The thickness of these 3 components of the metamaterial is up to 500 nm. They are supported by a macroscopic, rigid component for mechanical stability. The support can be a quartz window, a polished silica fiber tip, or the inner wall of a glass capillary (Fig. 1B). Examples of finished metamaterial surfaces on plates are shown in Fig. 2.

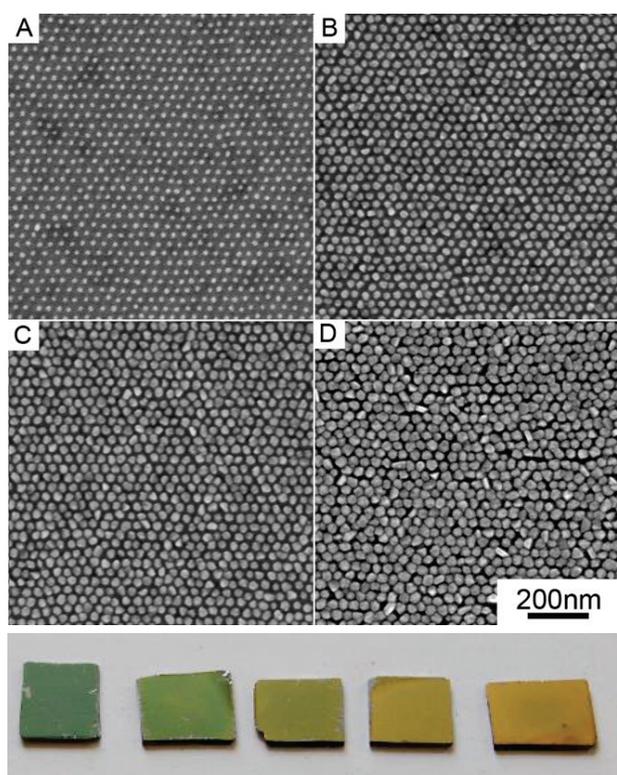


Figure 2: (TOP) SEM micrographs and (BOTTOM) optical images of metamaterial SERS substrates with varying gold nanoparticle diameter. These substrates were prepared on silicon wafer support.

3 SERS SENSOR INCORPORATED IN AN OPTICAL WINDOW

To simulate chemical sensing via SERS in a reaction chamber, the metamaterials were produced on 1-inch diameter, 1.66-mm thick quartz windows and seeded with

4-aminothiophenol (4-ATP) adsorbed as a monolayer on the gold nanoparticles. SERS spectra were collected using a LabRAM ARAMIS Horiba Yvon-Jobin Raman spectrometer, operating with a 633nm laser, in back-scattering mode. The main question addressed in this series of experiments is whether measurements through the optical window are consistent with data from the traditional, through air, SERS measurements. Thus, data collected with the laser incoming from the bare side (front illumination) of the quartz plate were compared to data collected with the laser incoming from the particle-coated side (back illumination) of the quartz plate.

The SERS spectra of 4-ATP are shown in Fig. 3 for front and back illumination. Qualitatively, the spectra of 4-ATP contain the same number of peaks and relative peak intensities regardless of the direction of illumination. The Raman signal of the quartz window is weak in this range of the spectrum and does not interfere with the SERS data analysis. Front illumination, where the light travels twice through the thickness of the quartz, actually leads to a stronger signal by a factor of ~ 2 . We estimate the enhancement factor to be 10^5 for this system.

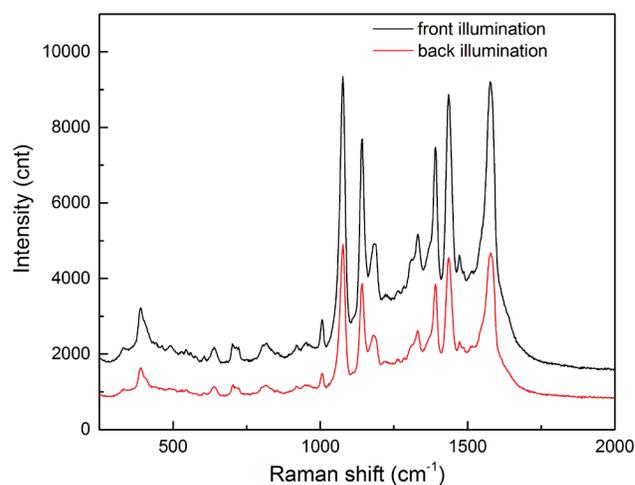


Figure 3: SERS spectra of 4-ATP recorded with front (black line) and back (red line) illumination of a quartz plate back-side coated with the metamaterial.

4 SERS SENSOR INCORPORATED IN A GLASS CAPILLARY TUBE

Most SERS based chemical detection systems are employed by spotting the analyte on a slide with metal nanostructures and transferring the slide to the Raman microscope. The slide is typically discarded after the single measurement. For process monitoring, in-situ, repetitive (high-throughput) sensing may be preferred. For example, a SERS sensor incorporated in a drain/exhaust pipe could be used to monitor by-products emitted from a reactor, waste water, etc. To simulate chemical sensing via SERS in a quasi-continuous manner, a flow-cell was built incorporating the metamaterials for SERS sensing in the

inner walls of glass capillaries (Fig. 4). While solutions of analytes were flowing through the capillary, a laser beam illuminated the metamaterial by travelling across the tube wall at normal incidence (Fig. 1B). The backscattered light leaving the tube was analyzed as a function of time to correlate the SERS signal with the composition of the solutions flowing through the tube.

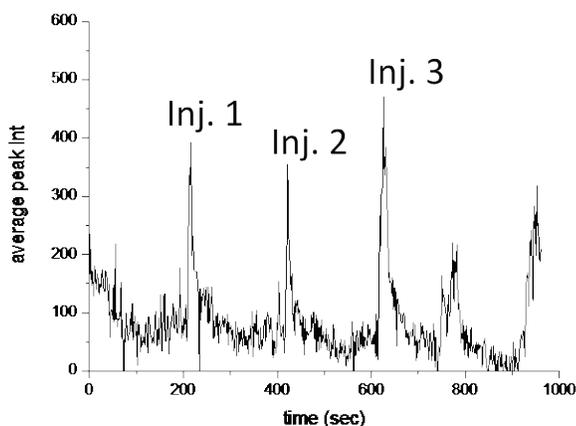
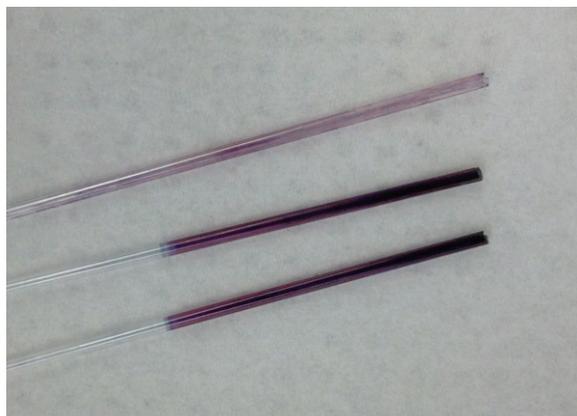


Figure 4: (TOP) Photograph of 3 capillary tubes for SERS measurements with different gold nanoparticle diameters. (BOTTOM) Plot of a SERS-signal transient (intensity-vs-time) from multiple injections of a Rhodamine6G solution in a flow cell containing the SERS capillary tube.

Fig. 4 shows a SERS-signal transient that illustrates the SERS sensor is able to report multiple exposures to a Raman-active molecule in continuous operation. In this experiment, the capillary was exposed alternately to aliquots of a Rhodamine-6G (R6G) aqueous solution and aliquots of a cleaning solution. The solutions were kept from mixing in the tubing of the flow cell system by incorporating an air bubble before and after each aliquot. The liquids and air bubbles were moved through the system using programmable syringe pumps. Every injection of R6G into the capillary tube is followed by a sharp increase in the SERS signal and the signal was pronouncedly reduced during every pass of the cleaning solution. The metamaterial was regenerated within minutes and the signal

intensity appears to maintain a narrow range. Interestingly, the highest intensity of SERS from R6G was obtained at times that correspond to the passage of the “trailing” air bubble through the capillary following the R6G exposure. This is in agreement with other observations with planar support substrates that show a stronger SERS signal when dry compare to when immersed in a solvent. This “delayed” appearance of the SERS signal in the transient response curve complicates the quantitative analysis of the performance of the system. The SERS enhancement factor and the limit-of-detection for particular analytes have not yet been determined.

5 SERS SENSOR INCORPORATED IN A FUSED SILICA OPTIC FIBER

The metamaterial was also produced on the polished tip of an optic fiber (Edmund Optics, 200 μ m core diameter 0.22 NA VIS/NIR fused silica fiber, polyimide coating) to demonstrate remote sensing by sending and receiving the optical signals through the fiber. The bare tip of the fiber was placed near the focal point of the objective lens (Olympus MPlan, 10x NA=0.25 WD=10.6 mm) of a LabRAM ARAMIS Horiba Yvon-Jobin Raman microscope, while the metamaterial functionalized tip of the fiber was immersed in the analyte solution. The fiber was ~0.5 meter in length.

There are a number of technical considerations specific to SERS measurements through optic fibers. First, the optic fiber can channel back to the spectrometer photons that originate from light sources other than the incident laser (e.g. sunlight, room lighting). Therefore, samples must be measured in the dark. Second, the fiber itself is a source of fluorescence and Raman scattering (Fig. 5). These features must be recognized in the recorded spectra and not mistaken for analyte signals. Therefore, the method is limited to analytes with Raman signals that do not overlap with the Raman signals of fused silica (420, 485, 600, and 790 cm^{-1}). The method also necessitates post-measurement analysis, such as background subtraction, peak fitting and principal component analysis. As shown in Fig. 5, large Raman shifts are preferred for sensing as they produce less fluorescence background. Third, this method is limited by the efficiency of inserting the incident laser light into the fiber and coupling the light scattered in the metamaterial back into the fiber. These losses were estimated by comparing the SERS signal measured when illuminating the bare tip and when illuminating the metamaterial-functionalized tip (Raman scattered light does and does not travel through the fiber, respectively). The SERS signals are lowered by a factor of ~15 due to fiber-coupling issues.

Despite the technical challenges listed above, remote detection of SERS-active molecules through the optic fiber is practical due to the tremendous enhancements in the Raman scattered light intensity by the plasmonic metamaterial, estimated in the order of 10^5 . Figure 6 shows the spectra of 4-ATP obtained by dipping the metamaterial-

functionalized fiber tip in an ethanoic solution of ATP. By comparing the analyte SERS spectrum with that of the bare fiber and the known spectrum of ATP, it is possible to unambiguously assign 5 Raman peaks (1075, 1140, 1390, 1435 and 1580 cm^{-1}) to 4-ATP adsorbed on the fiber tip. Efforts are underway to optimize the multi-layer film structure to maximize the SERS enhancement factor.

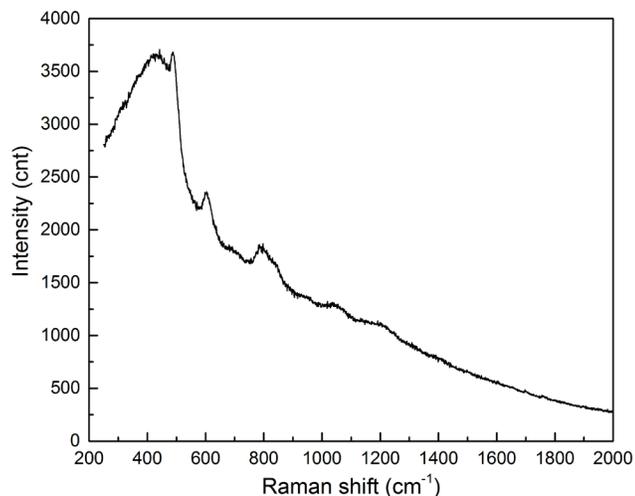


Figure 5: Raman spectra of a fused silica optic fiber illuminated by a 633 nm laser.

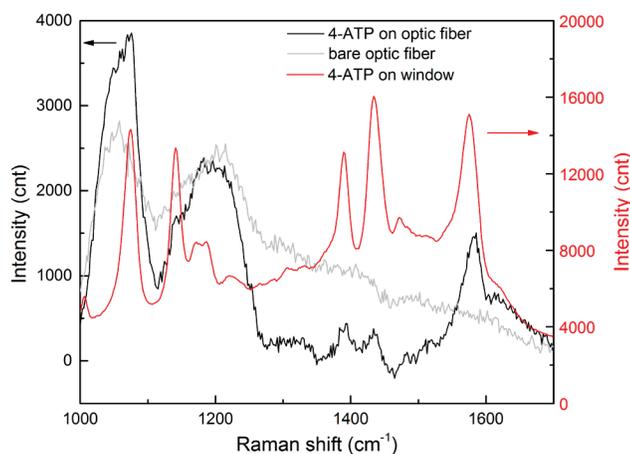


Figure 6: SERS spectra of 4-ATP recorded through a 0.5 meter long optic fiber (black line) and on a quartz window (red line) illuminated by a 633 nm laser. The Raman spectrum of the bare silica fiber is provided for comparison (grey line). Background subtraction was applied to address the optic fiber fluorescence.

6 DISCUSSION

Optical spectroscopy is a potent and versatile tool in analytical chemistry, however, Raman spectroscopy is infrequently the method of choice because of its low sensitivity. SERS, a nanotechnology-enabled method that

enhances sensitivity via plasmon-mediated interactions, has eliminated this limitation. Now, an engineering solution has been found to produce SERS substrates with reliable enhancement factors using the self-assembly of block copolymers and metal nanoparticles over multi-layer films. In this work, we have demonstrated that these metamaterials can be fabricated and supported on many components that are common in chemical reactors and optical sensors, such as plates, windows, tubes, and fibers. We have demonstrated the detection of Raman-active molecules at monolayer coverage level, equivalent to 10^{-16} - 10^{-14} mole, with lower detection thresholds possible. Because of the low cost of fabrication (self-assembly processes) the metamaterials are disposable, but we have also demonstrated quasi-continuous sensing using a cycle of dosing and cleaning steps that enables the use of the metamaterials in extended monitoring applications. Finally, we have introduced a metamaterial-based Raman optic fiber probe for remote sensing. There are potential in-vivo applications to this probe when the biochemistry of bodily fluids can be analyzed by Raman spectroscopy.

7 ACKNOWLEDGEMENTS

The authors are grateful to Dr. Seung Yong Lee of KIST (Seoul, Korea) for setting up the capillary tube flow-cell system. This work was supported by the National Science Foundation (Grant No. DMR-1151614) and by the UM Ventures Seed Grant Program (FY2016) of the University of Maryland.

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