Raman scattering has generated substantial interest as a spectroscopic technique owing to its generally well-resolved spectra that provide a unique fingerprint for every Raman-active substance or compound. Raman scattering is observed when light is inelastically scattered by molecular vibrational modes, resulting in a shift to both higher and lower frequencies. Surface-enhanced Raman scattering (SERS) is attributed to electromagnetic and chemical interactions between a surface with nanoscale metal structures and a target molecule adsorbed onto or in close proximity to the surface. The SERS effect can lead to a millionfold increase in scattering intensity over the relatively weak normal Raman scattering. Recent applications of SERS have included detection of cancer genes, glucose sensing at physiological concentrations, and detection of chemicals at the single-molecule level.

SERS active surfaces can be generated in a number of ways, including electron-beam lithography, nanosphere lithography, porous silicon, vapor-deposited metal islands, solgel-encapsulated metal colloids, and monolayer deposits of colloidal particles. However, these methods of fabricating roughened surfaces are either expensive or rely on self-assembled or randomly deposited structures that, by their very nature, have little sample-to-sample reproducibility. These difficulties have tended to limit the analytical use of SERS and have led to an ongoing effort to identify alternative substrates.

Optical fibers provide an attractive platform for SERS sensing because they avoid problems with free-space beams and optical alignment while being relatively cheap and easily obtainable. There have been a number of previous attempts to integrate SERS surfaces onto the distal tips of optical fibers in such a way that both the excitation beam and the scattered light are guided within the fiber. Although successful in generating a SERS response, these works generally rely on methods such as metal-island deposition to produce nanoscale roughness, and hence the fibers have the same fundamental problem of sample reproducibility. Polwartz et al. addressed this issue through the use of monolayer coatings of silver colloid but found approximately 10% deviation, which is still considered too high for fully quantitative analytical work.

Instead of using a standard single-core optical fiber, the research presented here concentrates on the use of imaging fibers. These fibers are typically made of between 1000 and 100,000 individual fibers (known as picture elements or pixels), drawn and fused together into a single bundle. Imaging fibers are commonly used in industrial or medical endoscopes to transfer images coherently between the input and output ends. It is well known that a selective etchant can be used to erode the individual picture elements to form wells with a reasonably regular, hexagonal close-packed pattern. The picture elements in commercial imaging fibers typically have a diameter greater than approximately 5 µm since the light-guiding capacity for visible wavelengths is reduced below this scale because of increases in radiation losses. The work presented here shows that drawing the imaging fiber to an even smaller diameter allows the wells and the cladding structures between them to be uniformly reduced to a nanoscale size suitable for use in SERS.

An imaging fiber with approximately 10,000 picture elements (FIGH-10-350S, 350-µm total outer diameter, Fujikura, Ltd.) was used for all the experiments. According to the manufacturer, these fibers are manufactured from synthetic silica glass cores with a fluorine-doped silica cladding. The imaging fiber bundles were cut into sections of approximately 100 mm. Acetone (puriss. ≥99%, Aldrich) was used to remove the protective silicone coating from the fiber. The fiber was held vertically and an oxy-acetylene torch was then used to heat the central section of fiber so that it was drawn down to a fine filament by a falling mass piece. The tapered fibers were then cleaved at a point at which the diameter was approximately 20–30 µm.

A buffered hydrofluoric acid (HF) solution consisting of 6 parts 40% ammonium fluoride (NH₄F) (Sigma), 1 part 49% HF (Asia Pacific Specialty Chemicals), and 14 parts 36.8% hydrochloric acid...
(HCl) (Merck) was used as the fiber etchant (i.e., \( \text{NH}_4\text{F}:\text{HF}:\text{HCl} = 5:1:11 \)). Buffered HF in combination with concentrated HCl has been shown to provide rapid and clean etching of silica imaging fibers.\(^{15}\) Samples of the drawn fiber were etched for periods of 1 and 2 min and then rinsed with de-ionized water. It is difficult to measure the depth of the etched structures directly, given the small scale of the fiber tips. However, atomic force microscope measurements on the unmodified image fiber suggest an etch rate of approximately 1.8–2.0 \( \mu \text{m/min} \) in the pixel cores. Although this figure might be modified by diffusion effects at smaller scales or in deeper wells, it provides an order-of-magnitude indication of the depth of the etched features.

The etched fibers were mounted onto a rigid support and then lightly coated with gold in a plasma sputter coater to permit scanning electron microscope (SEM) inspection in a Panasonic XL30. From the SEM pictures shown in Figs. 1–3 it is apparent that the cladding around each picture element etches at a slower rate than the silica core, resulting in a clearly defined honeycomb pattern. In addition, the outer cladding of the imaging bundle was retained, which helps to preserve the structural integrity of the etched tip. For both etch times the fibers show well-defined nanoscale structures suitable for use in SERS. Longer etch times lead to substantial erosion of the cladding material between the picture elements, which results in irregular pitting on the micrometer scale.

After SEM inspection, the 1- and 2-min etched fibers were coated with 100 nm of silver (high-purity Ag wire) in an Emitech K950X vacuum coater. The deposition was controlled by a quartz crystal microbalance (Emitech K150X). The coating did not substantially alter the appearance of the sample surfaces. Samples were then immersed in a 10-mM solution of thiophenol (99+%, Sigma-Aldrich) in ethanol (>99.7%, Merck) for 10 min, followed by a rinse in pure ethanol for 2 min. Thiophenol provides a convenient reference compound for SERS because it forms relatively stable monolayers on silver and gold metal surfaces.\(^9\) Raman spectra were obtained with a Renishaw System RM2000 fitted with a thermoelectrically cooled CCD detector. A Spectra-Physics Model 127 He–Ne laser (633 nm) was used to excite the spectra. The power at the sample was approximately 1 mW. A 20\(\times\) objective lens was used to project the beam onto the etched surface and collect the resultant Raman spectrum. In each case, five exposures of 10 s each were accumulated. Spectra were taken from the free surface rather than through the fiber because these hand-drawn fibers are sharply tapered and do not channel light efficiently. A more uniform fiber diameter can be obtained through standard commercial manufacturing techniques. This is expected to facilitate the internal excitation and collection of SERS spectra in future.\(^9\)–\(^{11,13,14}\)

The spectra obtained from the two samples are shown in Fig. 4, with the thiophenol SERS peaks clearly identified.\(^9\) The observed spectra suggest an enhancement factor of approximately \(10^6\) based on a comparison between the amplitude of the SERS peaks and the corresponding peaks of pure liquid thiophenol. The calculation of the enhancement takes into account the approximate number of molecules contributing to the Raman signal in each case. It was assumed that a monolayer of thiophenol was present on the planar dimension of the silvered surface, with...
a packing density of approximately 0.22 nm²/chain. The electromagnetic theory of the SERS effect shows that the size, shape, and aspect ratio of nanoscale metal particles are important factors in determining the enhancement produced by a substrate. The fiber etched for 2 min showed an additional gain of approximately 60% over the fiber etched for 1 min. The silver coating is unlikely to be continuous for well depths of 2 to 4 μm, but Fig. 3 suggests that there is sufficient structure on the walls around the wells to generate small differences in aspect ratio that might play a role in these results. In addition, there appears to be an increased background contribution between 1100 and 1600 cm⁻¹ in the more deeply etched fiber; the source of this has yet to be conclusively identified.

The work presented here has demonstrated that drawn imaging fibers can be used as SERS substrates. This is notable in that a functional nanoscale device has been produced without the need for expensive and complex processing equipment. This approach offers significant potential advantages through improved substrate reproducibility based on fine control of surface topography. Commercial optical fiber manufacturing techniques are well suited to the low-cost production of large lengths of material with uniform structural and optical properties. Further work is required to quantify the variability between samples, optimize the SERS enhancement, and improve the manufacturing process by performing controlled draws.

The SERS effect is a manifestation of the localized surface plasmon resonance, which also results in selective photon absorption. This raises the possibility of multiple transduction mechanisms based on these etched fiber structures. The fabrication of nanopoors is another area of current interest, with applications in catalysis, sensing, and the fabrication of optical and magnetic nanoparticles. Therefore it would be of fundamental interest to determine the minimum feature size that can be achieved with the method described here.

The authors thank Phil Francis of the Department of Applied Physics, RMIT University, for assistance with the SEM measurements and Kaushal D. Vora of the Industrial Research Institute Swinburne for assistance with the fiber etching. Paul Stoddart’s e-mail address is pstoddart@swin.edu.au.

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