

Nanostructured optical fibre for chemical sensing using surface-enhanced Raman scattering

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Abstract — To enable practical applications of surface-enhanced Raman scattering, we have constructed nanostructured surfaces with controlled geometry on the tip of an optical fibre. Preliminary results from commercially drawn SERS fibres are presented.

I. INTRODUCTION

Raman scattering has gained popularity as a spectroscopic technique due its well resolved spectra that provide a unique fingerprint for every Raman-active molecule. Raman scattering occurs when a molecule scatters incident optical radiation (usually from a laser) to both higher and lower frequencies. The shift observed is dependent on the structure of the specific molecule.

First observed in 1974 by Fleischmann *et al.* [1], surface-enhanced Raman scattering (SERS) can lead to an increase in the Raman signal by a factor of more than 10^6 . Such an enhancement allows for increased detection sensitivity or for shorter spectral integration times and lower excitation powers at a given analyte concentration. The SERS effect is attributed to the electromagnetic and chemical interactions that occur when a molecule and a metal surface with nanoscale roughness (10 - 100 nm) are in close proximity.

A significant ongoing effort to exploit the SERS process has resulted in notable recent developments, including the detection of glucose [2], cancers [3], biowarfare agents [1] and water quality monitoring [4]. However, more widespread application outside of the laboratory has been hindered by problems with reproducibility, stability and cost of overly delicate SERS substrates. In this paper we describe a robust and convenient optical fibre platform that may serve to overcome the drawbacks of the conventional substrates.

A. SERS Substrates

There are presently a number of methods for making nanoscale surfaces for use in SERS. These include lithographic techniques such as nanosphere lithography, e-beam lithography and UV lithography [5]. Colloidal solutions and random processes such as metal island film formation can also be used. These methods, however, are either too expensive or lack the reproducibility required for mass market applications.

The method presented here uses the etched and metal coated tip of a drawn imaging fibre to generate the nanoscale features.

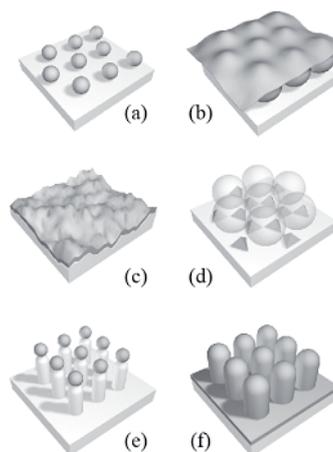


Fig 1: Common SERS substrates: (a) colloidal metal, (b) film over nanospheres, (c) roughened surfaces, (d) nanosphere lithography, (e) and (f) lithographically prepared surfaces.

B. Imaging fibre

Imaging fibres consist of a number (typically between 1,000 and 100,000) of optical fibres drawn into a coherent bundle in such a way that each fibre maintains its relative position throughout the length of the bundle. Imaging fibres are commonly used in medical appliances such as endoscopes.

It has been shown in a number of previous papers that by using a selective acid etchant, the cores of an imaging fibre can be eroded away to form wells [6]. The microwells formed in this manner have proven to have many uses in both chemistry and biology [7,8].

In order to transmit light efficiently, the cores of an imaging fibre typically have a diameter of greater than $3 \mu\text{m}$. Although this size is suitable for the microwell applications it is too large to act as an efficient SERS substrate. However, it has been demonstrated that when reducing the diameter of the cores and the spacing between them by a factor of 5 -10 before etching, the wells and the structures between them are reduced to the nanoscale, resulting in efficient SERS production [9]. This reduction is accomplished by drawing the whole fibre bundle to a smaller diameter.

II. NANOSTRUCTURED OPTICAL FIBRE

Different surface features can be produced by varying the diameter (and hence inter-core spacing) of the cores and varying the etch duration of the drawn fibres. The fibres shown in Fig. 2 were drawn by hand to have a range of inter-core spacings of between 250 and 420 nm before they were all etched for the same period of time.

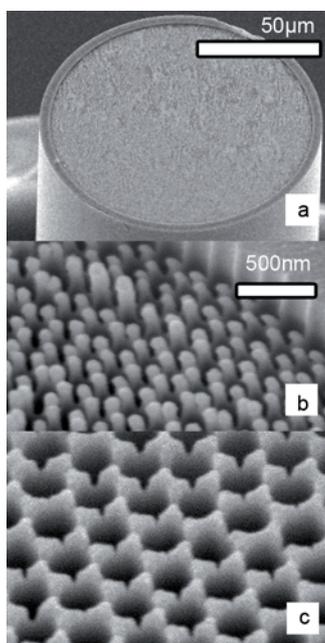


Fig. 2. (a) Drawn imaging fibre with an outer diameter of $110 \mu\text{m}$ and inter-core spacing of 450 nm (b) fibre with inter-core spacing of 250 nm producing rod structures and (c) fibre with inter-core spacing of 420 nm producing triangular structures. All fibres were etched for the same duration. Images were taken at an angle of 30° to the fibre axis to best illustrate the features.

After the structure is etched, it is coated with 100 nm of high purity silver as the SERS effect relies on having a nanostructured metal surface. A self-assembled monolayer of thiophenol ($\text{C}_6\text{H}_6\text{S}$) was then generated on the surface by soaking in a 10 mM solution in ethanol. Thiophenol was chosen as a standard analyte as it forms relatively stable bonds with silver or gold and produces a characteristic SERS signature, as shown in Fig. 3.

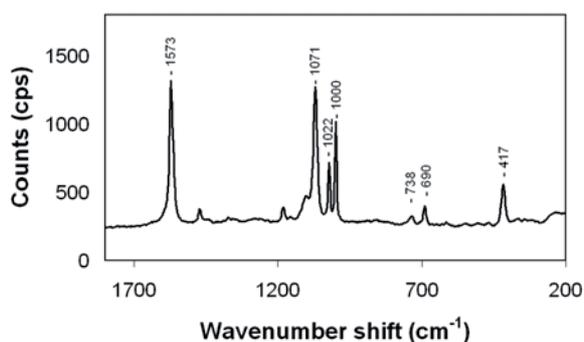


Fig. 3. SERS spectrum of thiophenol on a fibre with an inter-core spacing of 250 nm . The excitation wavelength used was 632.8 nm and the power at the sample was approximately $20 \mu\text{W}$.

The spectrum is taken by illuminating the tip of the fibre with the laser and collecting the signal via backscattering. At this stage, no measurements are taken through the fibre as these hand drawn fibres do not transmit light well. The enhancement factor is calculated by comparing the peak height of the 1000 cm^{-1} peak of the sample with that of pure thiophenol after normalising both the excitation power and the integration time.

The different surface structures produced (and illustrated in Fig. 2) give rise to different enhancement factors as shown in Fig. 4 (a). After extended periods of etching, the rod structures become progressively more elongated. Fig. 4 (b) shows how this change in aspect ratio alters the SERS enhancement factor. Varying both the inter-core spacing and etch duration makes it possible not only to create different surface structures but also different sizes of the structures. This flexibility allows the substrate to be optimised for different experimental conditions.

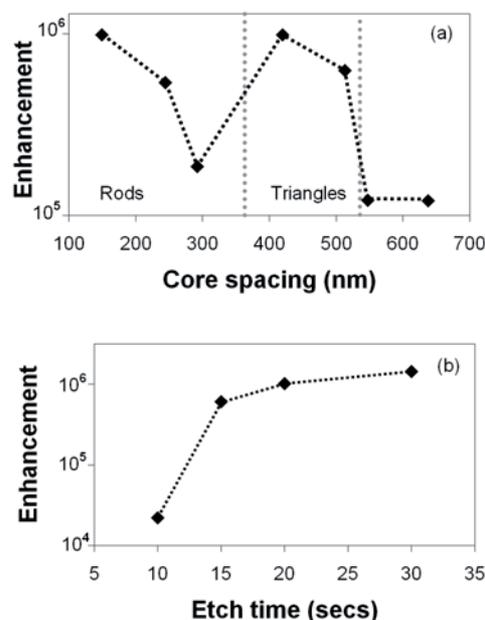


Fig. 4. (a) Variation of enhancement with different structures when etched for the same duration. (b) Variation of enhancement when etching a fibre with inter-core spacing of 250 nm for different periods of time.

One of the principle advantages of using an optical fibre as a SERS substrate is that long lengths of virtually identical material can be produced relatively easily. In order to test this, a length of imaging fibre was drawn at the Optical Fibre Technology Centre (OFTC) at the University of Sydney. The drawn fibre was found to have an inter-core spacing of approximately 450 nm . Nine samples were prepared and etched before the fibre was coated with 150 nm of gold. Once again, thiophenol was used as the reference compound.

The sensitivity of the etched fibres was assessed by extrapolating the sensitivity limit based on the signal level observed for the stable monolayer of thiophenol on the metal surface. For the gold probes, the sensitivity limit is found to

be equivalent to 0.004 of a monolayer, or alternatively, approximately 200 molecules per “nanoparticle” site. This preliminary result was achieved without any optimisation of etching and coating parameters. However, it is comparable to the attomole to zeptomole mass sensitivity reported for standard substrates [10].

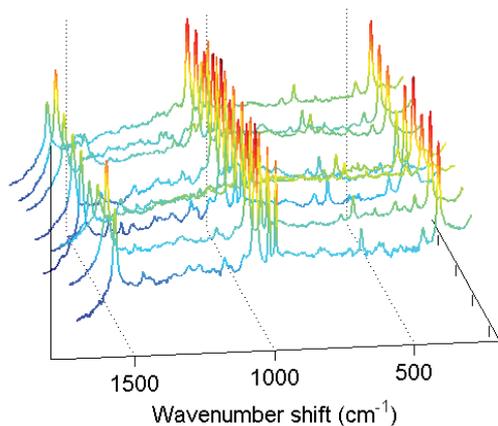


Fig. 5. Normalised spectra of thiophenol taken from nine different SERS fibre samples.

The repeatability of these nine samples was evaluated by determining the relative standard deviation (RSD) of the thiophenol peaks after normalisation to the 1000 cm^{-1} peak height. The RSD is a comparison between the average signal power of the peaks and their standard deviation. By this measure, the repeatability was found to be approximately 9%. This figure compares well with the 5% RSD reported for carefully controlled silver colloidal substrates [11] and is considerably better than the 20% RSD reported for mechanically roughened surfaces [12]. Further improvements may be possible with more careful control of sample positioning and more sophisticated spectral processing techniques. Although only a preliminary study, it shows that these SERS fibres have the potential to provide the repeatability required for accurate analytical measurements.

III. CONCLUSION

SERS substrates produced from the etched tips of drawn imaging fibres are shown to provide both high enhancement and high repeatability. Optical fibre chemical sensors are minimally invasive, inexpensive, stable and relatively robust. The image fibre approach allows sufficient flexibility for the system to be optimized for a range of experimental conditions that might be encountered in different application environments. Such substrates lend themselves to production on a commercial scale and this is currently being pursued.

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