Chemical sensors based on nanoparticle arrays

Paul R. Stoddart\textsuperscript{a}, Paul A. White\textsuperscript{b}, and Alex Mazzolini\textsuperscript{a}

\textsuperscript{a}Centre for Imaging and Applied Optics, School of Biophysical Sciences and Electrical Engineering, Swinburne University of Technology, PO Box 218, Hawthorn, Victoria 3122, Australia
\textsuperscript{b}CSIRO Manufacturing Science and Technology, Private Bag 33, Clayton South MDC, Victoria 3169, Australia

\textbf{ABSTRACT}

The size-dependent properties of nanomaterials are currently attracting a great deal of interest in the research community because of the many important potential applications in microelectronic, data storage and sensing devices. The signature optical property of metal nanoparticles is the localized surface plasmon resonance (LSPR), which occurs when collective oscillations of the conduction electrons are excited by light. The LSPR results in wavelength-selective photon absorption, scattering and local electromagnetic field enhancement. The latter contributes to the significant enhancements observed in surface-enhanced Raman scattering (SERS) and other surface-enhanced spectroscopies. Several groups have already demonstrated the enormous potential of compact, integrated SERS sensors for a broad range of chemical and biological sensing applications. However, the systems described so far have generally utilized substrates with a wide range of feature sizes and irregular spatial distributions. These factors contribute to relatively poor reproducibility between sensors. Fabrication techniques based on ordered, self-assembled arrays of nanospheres appear to offer a convenient and inexpensive means for generating uniform structures. Progress in applying these methods to the fabrication of reproducible SERS microsensors will be described.

\textbf{Keywords:} nanoparticles, localized surface plasmon resonance, surface-enhanced Raman scattering, self-assembly, nanosphere lithography, chemical sensing

1. INTRODUCTION

The new science of nanotechnology has largely been driven by the unique and sometimes unforeseen properties of aggregates of atoms and molecules on the mesoscale (between one and a few hundred nanometers)\textsuperscript{1}. There is a great deal of interest in exploiting the new properties and behavior of single materials or combinations of components to generate so-called smart structures or systems. Given that the physical properties of smaller devices are generally more susceptible to alteration, they are particularly attractive for sensing applications\textsuperscript{2}. In the present work we describe a potential application of the size-dependent optical properties of metallic nanoparticles for chemical sensing.

The localized surface plasmon resonance has been described as the signature optical property of metallic nanoparticles\textsuperscript{3}. This phenomenon occurs when nanoparticles of certain metals (primarily silver, gold and copper) are illuminated with light of the correct wavelength to excite collective oscillations in the plasma of conduction electrons. One of the consequences of the LSPR is the generation of an enhanced electromagnetic field in the near surface region of the nanoparticle. The amplified electromagnetic field contributes to the significant enhancements observed in surface enhanced spectroscopies\textsuperscript{4,5}. As such, surface enhanced Raman scattering is perhaps the best known of the many interesting effects associated with the LSPR\textsuperscript{6}.

Raman scattering is observed when light is inelastically scattered by vibrating molecules, resulting in a shift to both higher and lower frequencies. Scattering may be enhanced by a factor greater than $10^6$ for molecules adsorbed on a surface containing gold or silver nanoparticles. In this way, even 1% of a monolayer of molecules adsorbed at a SERS-
active surface may be detected. The Raman-active vibrational frequencies of the molecules provide a characteristic fingerprint for the species present and a sensitive probe of the molecular environment. Raman spectroscopy is uniquely suited to investigate samples of virtually any kind, including gases, solutions, solids, and both clear and turbid media.

The traditional types of substrate used for SERS have tended to contain a wide distribution of particle sizes with generally poor reproducibility and stability. The distribution of particle sizes is believed to reduce or mask the expected particle-size dependence of the peak excitation wavelength for the LSPR4. Therefore it appears that ordered nanostructures with uniform size distributions comprise an attractive class of substrates. Improved preparation of SERS substrates, together with progress in spectroscopic techniques, has driven renewed interest in the field6.

A variety of techniques for building structures smaller than 100 nm have been proposed. Regular arrays of silver particles have been deposited on silica posts that were fabricated by standard techniques of photolithography7. More recently, e-beam lithography has been used to obtain a greater variability in the structural parameters of particle arrays8. However, the limited resolution of the former technique and the high sample cost of the latter have limited their use. A technique known as nanosphere lithography comprises an alternative “bottom-up” approach9. In this case, a metal film is deposited over a self-assembled periodic array of polymer nanospheres. Triangular metal nanoparticles are formed on the substrate through the interstices of this mask and remain on the substrate after the nanospheres are removed. Particles in the range 20 – 1000 nm can be obtained, which comfortably covers the size distribution suitable for SERS. Moreover, the SERS signal can be optimized for a particular target molecule by changing the nanoparticle aspect ratio and local dielectric environment9. All of the above methods for generating SERS substrates have confirmed that improved and reproducible SERS enhancements can be obtained with optimized periodic structures.

Improvements in the preparation of LSPR systems are of particular interest for the development of optical fiber sensors. The use of optical fibers to deliver the laser beam to the sample and to collect the resulting Raman signal has allowed the on-line monitoring of industrial processes10. It has been recognized that the combination of fiber-optic probes with the high sensitivity and specificity of SERS potentially allows powerful chemical sensors with low cross-sensitivities11. In general, reproducible and tunable SERS-active fiber probes would have a number of additional advantages for the development of chemical sensors:

- The small size and flexibility of optical fibers allows highly localized and minimally invasive monitoring. The low cost and non-invasive nature of the probe element allows contaminated or faulty sensors to be conveniently replaced. This also implies that the main difficulty with conventional transducers may be avoided, in that completely reversible bonding of the detectable particle to the sensor-active coating and completely irreversible chemical bonding of this sensor-active coating to the transducer is not necessarily required12. The SERS spectrum itself provides a convenient internal measure of sensor performance and data integrity. This might even allow routine high-throughput analyses.

- Raman spectroscopy is a highly specific transduction method for monitoring changes in chemical composition and identifying multiple analytes. Raman spectroscopy is particularly effective with organic compounds and in an aqueous environment. A reproducible SERS effect should allow more accurate quantitative measurements of concentration.

- A variety of ultrathin surface layers can be applied to individual sensors in order to tailor their response. In this way trace analytes can be concentrated by selectively adsorbing receptor molecules and an array of sensors can readily be assembled13. Optical fibers are amenable to the development of multi-mode sensor assemblies, while bundles of fibers could be used for chemical imaging.

In the past, Raman spectroscopy required bulky but delicate equipment to acquire the relatively weak signal. A number of technological improvements over the last decade have combined to enable the development of increasingly compact, rugged and automated Raman instrumentation10. A compact, reliable laser source and scientific CCD detector are now typically combined in a fiber-coupled instrument. These factors, together with the inherent advantages of the Raman technique, have led to its rapid deployment in a wide range of chemical measurement applications.

Researchers have successfully used a variety of methods to generate inhomogeneous SERS-active fiber tips11,14-16. However, the limited available data suggests that the sensor-to-sensor reproducibility of these devices is rather poor.
Within the same batch of sensors, Viets and Hill report standard deviations in SERS intensity ranging from 20% to 42% for various preparation methods\textsuperscript{11}. The situation can be improved by immobilizing colloidal silver particles on the fiber tip\textsuperscript{14}. This yields a variability of approximately 10% at the 95% confidence level, which is still considered insufficient for analytical use.

To the best of our knowledge, none of the optimized periodic SERS structures have been exploited in the optical fiber systems yet. It is clear that substantial technical barriers restrict the use of standard lithography techniques in this case. However, we believe that nanosphere lithography offers an accurate, versatile and inexpensive solution to the mass production of high-quality periodic particle arrays (PPAs) on the tips of optical fibers. In this paper, we describe our efforts to develop a simple, robust and convenient method for generating reproducible and tunable SERS substrates on optical fibers. Surface enhanced Raman spectra obtained from relatively large areas of PPA on planar surfaces are reported, together with the results of initial efforts to coat individual fibers. The outlook for extending nanosphere lithography to the tips of optical fibers is discussed in conclusion.

2. METHODOLOGY

A monolayer film of nanospheres (e.g., polystyrene, PMMA, silica) is typically obtained by inducing a solution to evaporate on a substrate. As long as the nanospheres are able to diffuse freely across the substrate, they will seek their lowest energy configuration and self-assemble in a hexagonally close-packed pattern. Methods through which this can be achieved include spin coating\textsuperscript{3}, drop coating\textsuperscript{17} and thermoelectrically cooled angle coating\textsuperscript{18}.

Once a layer of nanospheres is obtained on the surface of interest, nanosphere lithography is performed by depositing a thin film of metal by physical vapor deposition from a source normal to the substrate. The nanospheres can subsequently be removed by sonicating the entire sample in a solvent, leaving behind a regular array of material deposited through the interstices of the nanosphere mask. An in-plane particle diameter of about 80 nm can be achieved using 350 nm spheres\textsuperscript{3}. A variety of defects can occur in the self-assembled film. Most notably these include polycrystalline domains and packing defects along the domain boundaries, vacancies and line defects. In Ref. 18, it is argued that the quality of the film depends on the properties of the substrate, the homogeneity of the evaporation process and the range of particle sizes.

In order to identify a simple yet robust method for generating PPAs on optical fibers, we initially tried a simple “dip and dry” method for coating both cleaved and polished fibers. We then proceeded to investigate the effect of the spin coating and angle coating methods on the evaporation process. In an effort to reduce the defect density to an acceptable level, these studies were focused on smooth, clean planar glass substrates and a relatively monodisperse nanosphere suspension.

2.1 Materials

Inexpensive commercial silica fibers are well suited to Raman spectroscopy as they show minimal transmission losses and negligible fluorescence. The optical fiber used in this work was a hard clad silica multimode fiber with core diameter of 200 µm (FT-200-UMT, Thorlabs). This fiber was used out of convenience: a low OH fiber, optimized for transmission in the visible to near infrared, would be preferable for Raman spectroscopy at red or near infrared wavelengths.

Short sections of these fibers (ca. 15 cm) were dip coated with 350 nm polymethyl-methacrylate (PMMA) nanospheres in an aqueous suspension (ME-2200, 18wt%, Soken Chemical and Engineering Company). The SERS measurements were performed with films assembled on borosilicate glass microscope slides. The planar substrates were prepared with 350 nm diameter (nominal) polystyrene nanospheres in aqueous suspension at 10% solids by weight. These particles, supplied by Duke Scientific Corporation, have a certified mean diameter of 343±9 nm.

Trichloroanisole (1,3,5-trichloro-2-methoxybenzene, ≥99.6% GC) and ethanol (puriss., ≥99.8% GC) was purchased from Riedel-de Hähn; thiophenol (benzenethiol, >99%) was obtained from Aldrich and sulfuric acid (puriss., 95-97%) from Fluka. All chemicals were used without further purification. High purity water with resistivity of 18 MΩ was produced by a Millipore Milli-Q water purification system.
2.2 Preparation of substrates

Optical fibers were polished by hand using a sequence of 9, 3, 0.3 and 0.05 µm aluminum oxide lapping film discs (Precision Surfaces International). In general, our aim was to achieve surfaces with a characteristic roughness scale much smaller than the nanosphere diameter. It is clear that the self-assembly process will be ineffective if this condition is not met. Cleaving of optical fibers was performed using an Erem FO1 cleaving tool designed for 250 µm fibers. In order to obtain a clean and hydrophilic surface, the glass slides were soaked in pure sulfuric acid for 24 hours. They were then rinsed and preserved in ethanol until use.

Spin coating was performed with a P6708 programmable spin coating system from Specialty Coating Systems. The homemade angle coating system consists of a small plastic box and a Peltier cell (Melcor). In our set-up, the Peltier cell was used to alter the drying time, but can also be used to improve the film quality by maintaining a stable temperature18. The small volume of the plastic box may also serve to slow down the evaporation process if necessary and protects the surface from external airflow and particulate contamination. The polystyrene nanospheres were used both as received and diluted in a ratio of 1:5 with pure water to investigate these coating methods.

Gold films were vapor deposited by means of an Emitech K950x Turbo Evaporator. The unit includes a quartz crystal microbalance (Emitech K150x Film Thickness Monitor) for monitoring the film thickness. In practice, the film thickness was determined by calculating the approximate length of wire (0.2 mm diameter high-purity Au wire from ProSciTech) required to achieve a desired layer thickness. The thickness of metal on the actual substrate was confirmed by means of atomic force microscopy.

Thiophenol was chosen as a convenient reference chemical to test SERS activity because it is expected to form stable, chemically bonded monolayers on gold surfaces. A glass substrate with a 55 nm layer of gold was immersed in a 10 mM solution of thiophenol in ethanol for 10 minutes and was then rinsed with ethanol. Trichloroanisole (TCA) is a volatile compound that is commonly associated with cork taints in wine. Recent research has indicated that wines exhibiting cork taint may have low or chemically undetectable concentrations of TCA19. A substrate with a 52 nm layer of gold was exposed to the saturated vapor above a 400 ppm solution of TCA in ethanol. The Raman activity was measured in situ through a transparent polymer film that was found to make no apparent contribution to the spectrum.

2.3 Instrumentation

AFM measurements were performed with an NT-MDT Solver LS scanning probe microscope. All measurements were performed under ambient conditions in semi-contact mode with an etched silicon cantilever (Ultrasharp noncontact “golden” silicon cantilevers, NT-MDT). The probe tips have a vertex angle of 22˚ and radius of curvature smaller than 10 nm; their resonant frequencies are between 150 and 200 kHz.

Raman spectra were obtained using a Renishaw System RM2000, fitted with a thermoelectrically cooled, NIR enhanced (deep depletion) CCD detector. A SpectraPhysics Model 127 helium-neon laser (wavelength 633 nm) was used to excite the spectra; this was filtered by a notch filter to reject plasma lines. Samples were examined under an Olympus BH2 microscope, which allowed the selection of suitable sample regions. Spectra were collected from the selected region in a back scattering geometry through a ×5 MD Plan objective (NA 0.12, working distance 13.2 mm). This objective, with its relatively large focal spot of about 20 µm, was used to reduce heating of the surface. The laser power at the sample was about 1 mW; integration times were 30 seconds with five accumulations in each case.

3. RESULTS

Cleaving can provide a clean, mirror-flat and perpendicular surface that may be directly suitable for nanosphere lithography in small diameter fibers. However, we found that flat surfaces were difficult to achieve on the 200 µm fibers. This leads us to conclude that polishing is a more attractive approach to surface preparation. Polishing has the added advantage that many fibers can be polished to the same height and then coated simultaneously. This should lead to economies of scale in eventual manufacturing. Scanning electron microscopy (SEM) and optical microscopy showed that some minor residual scratches were left after the 0.05 µm polishing step. This suggests that, with some further development, the polishing procedure can deliver an acceptable surface quality for nanosphere lithography.
A fiber tip was dipped into a suspension of 350 nm PMMA nanospheres and then flicked to remove excess material and dry the coating. The general results of this simple method can easily be assessed under an optical microscope, because interference between the plane parallel layers results in a variety of characteristic colors. Therefore, one can readily distinguish between uncovered glass, monolayers, bilayers and even thicker layers. A typical result is shown in Fig. 1. Although this gray scale reproduction does not have the clarity of the color micrograph, regions of bare glass (a), monolayer (b) and thicker layers (c) are readily apparent. A thick crust of excess material is left on the buffer layer surrounding the 200 µm glass core. The differentiation between single, double and thicker layers is even clearer in the inset image. Although there is a relatively large area of monolayer, it tends to be rather imperfect with limited areas of defect-free coverage. Note also the line defect in the monolayer area caused by a polishing scratch (indicated by the arrow). Although the surface preparation needs further refinement, the small number of these substrate related defects confirms that the polishing procedure is fundamentally sound.

![Fig. 1: A polished fiber tip coated with PMMA nanospheres by the “dip and dry” method (see text). Regions of bare glass (a), monolayer (b) and thicker layers (c) can be seen. The arrow points to a line defect in the monolayer caused by a polishing scratch.](image)

It was possible to obtain a somewhat more even coverage using a diluted solution of the PMMA nanospheres. However, the particles then tend to agglomerate, perhaps due to dilution of the surfactant that is used to maintain this particular colloidal suspension. Although recent results suggest that this type of coating would probably generate a SERS response\textsuperscript{11,15}, it is clear that repeatability between different fibers would be poor.

As this simple “dip and dry” approach appears unlikely to generate reproducibly coated fibers, it was decided to investigate the more conventional spin coating and angle coating methods. The initial experiments with spin coating were disappointing. The glass substrates were spun at speeds between 120 rpm and 600 rpm for several minutes. Some difficulty was experienced in achieving a suitable degree of spreading. If the rotation speed is too high, the suspension is rapidly thrown off the substrate and coverage is very low; if the rotation speed is too low, no spreading occurs. A delicate balance must be struck between the various attractive and repulsive forces that regulate the interaction between the particles and the substrate. Self-assembly is therefore a complex, materials dependent process. Moreover, it would be relatively difficult to integrate a bundle of optical fibers into the spin coater geometry.

On the other hand, initial results from the thermoelectrically cooled angle coating method were encouraging. Large domains of good quality monolayer can be achieved on planar glass substrates, tilted at an angle of about 7°. A reasonable coverage (about 2 cm\textsuperscript{2} for 0.5 mL of suspension) can be achieved by adjusting the inclination of the substrate by eye. A typical coating, as shown in Fig. 2, delivers good quality monolayer regions that extend over hundreds of micrometers, although the crystal domain boundaries (the faint vertical lines in the figure) confine the low-defect monocry stalline zones to tens of micrometers. In order to provide some visual contrast, Fig. 2 includes two
“boomerang” shaped features. These are probably associated with dust particles or clusters of spheres that disrupt the drying process of the layer. The drying was directed from top to bottom of the image, in accordance with the slope of the substrate.

These results suggest that angle coating might more easily render good quality nanosphere monolayers than spin coating. Nevertheless, it is well established\(^3\) that spin coating can also generate defect-free domains in the range 10-100 \(\mu m^2\) and so this method should not be neglected. The angle coating results are significant in that the good quality monolayer now extends over an area comparable to the tip of an optical fiber (or a bundle of several fibers). Note that defect-free coverage of a fiber tip is unlikely ever to be attained. However, the relatively minor defects that occur in a good quality region of monolayer (such as that shown between the boomerang features of Fig. 2), will have a statistical effect on the SERS activity that should be reasonably reproducible from one fiber to the next.

Fig. 2: A monolayer of nanospheres formed on a glass substrate by thermoelectrically cooled angle coating. The thicker “boomerang” shaped defects are believed to be caused by dust particles or agglomerations of nanospheres. The faint vertical lines are associated with crystal domain boundaries.

The nanoscale topography of the monolayer regions found in the angle-coated samples was investigated by means of AFM. Large- and small-scale images of a typical nanosphere array are shown before gold coating in Figs. 3(a) and 3(b) respectively. The large-scale image exhibits several of the typical defects described above. It is interesting to observe the apparent anisotropy of the spheres, as shown in Fig. 3(b). We believe that this is caused by the surfactant residue that remains after the water has evaporated. The residue dries inhomogeneously because of the drying direction imposed by the inclination of the substrate. Drying takes place along a horizontal border that is perpendicular to the inclination direction. The appearance of the nanosphere array remains virtually unchanged after coating with a 50-70 nm layer of gold.

Unfortunately, the presence of the surfactant residue between the nanospheres appears to disrupt the lithography process. After coating a substrate with a 52 nm layer of gold, the nanospheres were removed by sonication in ethanol for 15 minutes. AFM images were taken of previously noted monolayer regions, but there was no evidence of the characteristic triangular Au nanoparticles produced by nanosphere lithography. It appears that the residue completely blocks the gaps between the spheres, thereby preventing adhesion of any metal to the glass substrate. The absence of discrete metal particles would be expected to have a significant impact on the level of SERS activity, as any enhancement must now be generated by the relatively modest “roughness” of the Au film.
A thin layer of gold was deposited over two angle-coated substrates so that the SERS activity of the monolayer structures could be investigated. One substrate was exposed to thiophenol, while the other was exposed to trichloroanisole, as described in Sec. 2.2. In each case, Raman spectra were gathered from an area of gold-coated monolayer nanospheres and compared against a nearby region of gold-coated glass (i.e. a portion of the substrate that had not been coated by nanospheres). The spectra are shown below in Fig. 4. The gold film over nanospheres (AuFON) clearly enhances the Raman signal in each case. The thiophenol spectrum is complicated by the presence of additional peaks at about 1390, 1660, 1700 and 1765 cm$^{-1}$. These peaks do not appear to experience the same degree of enhancement as the peaks that have previously been ascribed to thiophenol$^{11}$ (compare with the enhancement for the main thiophenol peaks, which are marked by the bars in Fig. 4(a)). An enhancement factor of about 20 was obtained for

![Fig. 3: AFM images of a monolayer nanosphere array formed by angle coating. The anisotropy of the structure is more easily discernable in the magnified image (b).](image1)

![Fig. 4: Raman spectra obtained from gold films over nanospheres and gold films over glass. The angle-coated substrates were exposed to (a) thiophenol, and (b) trichloroanisole.](image2)
the thiophenol spectra by taking a ratio of the peak heights at 1575 cm\(^{-1}\). In contrast, no spectral features can be discerned for the gold film on glass exposed to TCA.

Although an enhancement factor of 20 appears relatively poor in comparison to values of about 10\(^6\) quoted in the literature, it must be remembered that these structures are by no means optimized. The absence of the triangular Au nanoparticles, which are a specific goal of nanosphere lithography, is probably the most significant contributing factor. Several additional parameters can effect the SERS enhancement, ranging from the thickness of the gold film and the size of the nanoparticles, through to the geometry in which the spectrum is obtained. The use of more appropriate nanosphere suspensions and a more systematic study of these various parameters should yield a more reliable enhancement factor.

4. CONCLUSION

After rejecting the simple “dip and dry” method, we have attempted to evaluate the somewhat more sophisticated spin coating and angle coating methods for producing periodic particle arrays on the tips of optical fibers. Initial results have been more favorable for the angle coating method, where we have obtained relatively large areas of high quality monolayer coating of planar glass substrates. These comprise regions that extend over distances on the order of hundreds of micrometers, where the effects of defects can be considered on a statistical basis. In comparison with spin coating, the simple geometry of the angle coating method also seems more applicable to optical fibers. It may also be possible to scale up the process by angle coating bundles of optical fibers that have been polished to a common height.

The SERS results presented here confirm the remarkable sensitivity of the technique, especially considering that the Au layer was by no means optimized. In particular, the triangular metal nanoparticles, with their desirable LSPR properties, were not formed in this case. The AFM results indicate that this aspect of the process can be improved by using nanosphere solutions that leave little or no residue on drying. Therefore, while considerable work remains to optimize the nanosphere lithography process for angle-coated substrates, the potential for applying this technique to optical fibers is very encouraging.

SERS is now considered one of the important phenomena of both surface science and nanoscience. However, its exploitation in practical sensing systems has been hindered by the lack of reproducible and homogeneous SERS-active surfaces\(^6\). If we are able to manufacture reproducible and tunable PPAs on the tip of a fiber using nanosphere lithography, it will become possible to mass-produce cheap and versatile SERS probes. In this way, we hope to develop an effective platform that will allow many new applications to be addressed in chemical sensing.

We note that the PPA fiber optic sensing elements discussed here are also likely to be compatible with other proposed sensing mechanisms. There are at least four other nanoparticle-based sensing mechanisms that can transduce chemical interactions into optical signals. These are based on changes in the LSPR extinction or scattering intensity, shifts in the maximum wavelength (\(\lambda_{\text{max}}\)) of the LSPR, or combinations of these (see Ref. 17 and references therein). Recently, Haes and Van Duyne have demonstrated that the LSPR \(\lambda_{\text{max}}\) of silver nanoparticles - obtained via nanosphere lithography on glass substrates - can shift in response to local refractive index changes and charge-transfer interactions\(^{17}\). They claim that an extremely sensitive and selective nanoscale sensing mechanism can be achieved in this way. The wavelength shifts can be observed using simple equipment for UV-visible extinction spectroscopy, which would greatly facilitate field-portable environmental or diagnostic applications. The availability of low-cost, parallel arrays of optical fibers will have a significant impact on such applications.

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