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Short communication

Nanoimprinted optical fibres: Biotemplated nanostructures for SERS sensing

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ABSTRACT

Optical fibre surface-enhanced Raman scattering (SERS) sensors offer a potential solution for monitoring low chemical concentrations in remote or in situ sensing scenarios. The SERS effect relies on the interaction of analyte molecules with nanostructured metal surfaces. We demonstrate a nanoscale biotemplating approach to fabricating these sensors, using nanoimprint lithography to replicate cicada wing antireflective nanostructures onto the end faces of standard silica optical fibres. These SERS-compatible nanoarrays are coated with silver to make them SERS active, and thiophenol and rhodamine 6G are used as test analytes, from which strong SERS spectra are collected using both direct endface illumination and through-fibre interrogation. This combination of biological templates with nanoscale replication and optical fibres demonstrates a high-resolution, low-cost approach to fabricating high-performance optical fibre SERS sensors.

1. Introduction

Nanoimprint lithography (NIL) has shown itself to be a powerful tool for replicating arbitrary micro and nanoscale surface relief patterns. Its high resolution, high throughput and low cost have made it a highly regarded and highly accessible nanofabrication technique. One application that demands the high precision nanoscale fabrication provided by NIL is that of surface-enhanced Raman scattering (SERS).

Surface-enhanced Raman scattering exploits the intense near fields at the surfaces of plasmonically active nanostructures to enhance the normally weak Raman scattering cross-sections of most molecules. These enhancements, which can be six orders of magnitude or greater, have made SERS a powerful tool for detecting low concentrations of many chemical and biological substances (Cao et al., 2002; Grow et al., 2003; Haynes et al., 2005; Vo-Dinh et al., 2002). However despite its usefulness, SERS is generally limited to laboratory use due to the lack of affordable, reliable and simple to use substrates. Furthermore, while typical SERS surfaces are formed on planar substrates such as glass slides, there are many instances such as remote and in vivo detection where a small, robust and implantable sensor is preferred. It is for these reasons that research has been conducted into the fabrication of SERS capable surfaces on the tips of optical fibres. To date, there have been several attempts in this direction (Viets and Hill, 1998). Simple metal coating of mechanically roughened tips (Mullen and Carron, 1991), metal island formation by slow evaporation (MacDonald et al., 1994), colloidal mask coatings (Stokes and Vo-Dinh, 2000) and the immobilization of metal colloidal particles (Polwart et al., 2000; Shi et al., 2008) have all shown potential. However these techniques rely on fundamentally random formations and as such, have intrinsically limited reproducibility. A recent innovation has demonstrated greater control of its nanostructures by chemically etching drawn imaging fibres (White and Stoddart, 2005), however these have not yet proven suitable for through-fibre sensing.

An alternative probe design presented in this work is based on the polymer replication of nanostructured templates. It was recently demonstrated that NIL can be applied to the endface of an optical fibre (Viheriala et al., 2007; Scheerlink et al., 2008), where sub-micron structures with features of the order of 250 nm and 630 nm were replicated respectively. In this paper, we demonstrate the use of NIL to fabricate a nanoscale SERS structure on the endface of an optical fibre.

As a matter of convenience, the SERS nanostructures are derived from a biological source. Photonic structures in biological organisms are often startling in their complexity and accomplishment. Prime examples are the multilayer structures on the wings of Morpho butterflies (Vukusic and Sambles, 2003) and the nanoprotuberance antireflection arrays found on the corneas of butterflies (Stavenga et al., 2005) and on the transparent wings of some hawk

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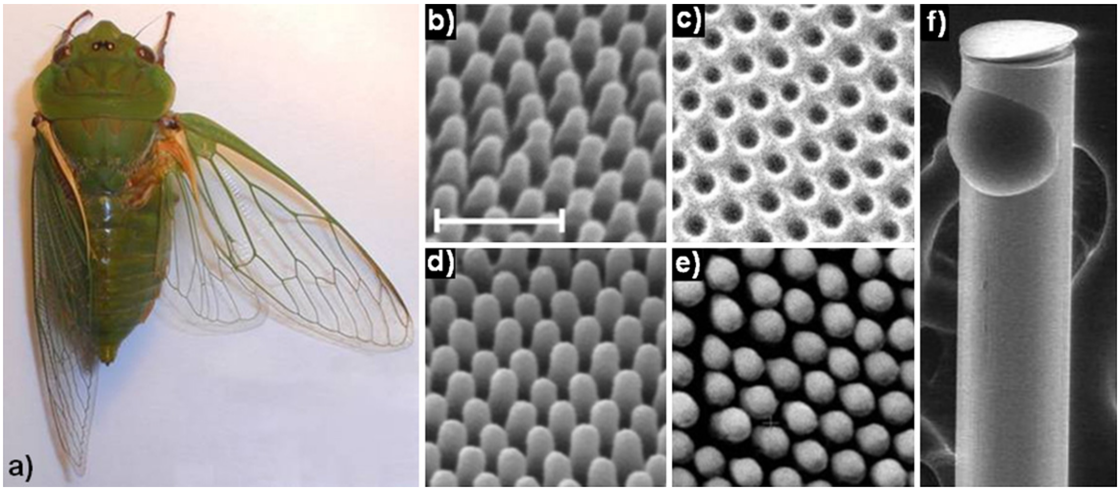

Fig. 1. A photograph of (a) the Australian greengrocer cicada is shown, alongside SEM images of (b) the cicada wing nanotemplate (c) the inverse h-PDMS mold (d) the polymer replica on an optical fibre endface (e) the silver coated replica and (f) a macroscopic view of the imprinted optical fibre. Scale bar is 500 nm.

moths (Yoshida et al., 1997) and termites (Watson and Blach, 2002). In this instance, the chitin antireflection structures on the surface of cicada wings (Stoddart et al., 2006) are used as nanostructured templates.

The nanostructure on a cicada wing consists of a dense two-dimensional array of pillars that have separations, diameters and heights of approximately 50 nm, 110 nm and 200 nm, respectively, as shown in Fig. 1. These pillars have approximate hexagonal distributions within micron-scale domains. Previous works have independently shown that these cicada wings are suited to direct use as efficient SERS substrates (Stoddart et al., 2006) while another group has shown that they are suited to replication (Zhang et al., 2006; Xie et al., 2008). Here, we use nanoimprint lithography to integrate the cicada nanostructure onto an optical fibre platform, and in doing so, demonstrate a capability for producing compact, low cost and high sensitivity SERS sensors.

2. Materials and methods

2.1. Nanostructured mold

The Australian greengrocer cicada "*Cyclochila australasiae*" was used for this work. Fabrication of a mold began by segmenting its wings into 9 mm^2 sections to exclude untextured venation, as illustrated in Fig. 2a, before they were drip coated on one side with h-PDMS elastomer solution. The h-PDMS was prepared as specified in the literature (Kang et al., 2006), and takes the form of a low viscosity liquid after mixing. The coated wings were then degassed in vacuum for 10 min to promote filling of the nanostructure, before being placed coated side down onto a glass wafer. Thermal curing of the h-PDMS was then performed by heating the glass wafer on a hotplate at 60 °C for>12 h. A scalpel blade was then used to pry one edge of the flexible wing segment upwards, at which point the entire wing piece snapped free with very little resistance, leaving the cured h-PDMS cast bonded firmly to the rigid glass backing. This separation process was conducted at the curing temperature in order to avoid differential thermal expansion and the associated potential for damaging the cast (Schmid and Michel, 2000).

2.2. Optical fibres

The optical fibres used in this demonstration were arbitrarily selected 50/125 μm graded-index multimode fibres. These were stripped of their jackets and then cleaved to produce flat endfaces at both the proximal and distal ends of the fibre. Since these fibres are used in the optrode configuration, wherein they carry both the excitation source and Raman scattered light, the cleaved lengths were kept short, as is common practice in the literature (Polwart et al., 2000; Viets and Hill, 1998, 2000a,b), in order to minimize the background Raman contribution from the fibre itself (Ma and Li, 1996).

While background Raman contributions can be managed by the subtraction of reference spectra (Viets and Hill, 2000a), short SERS probes could find direct utility in interfacing to conventional fiber-coupled remote-sensing Raman systems, which typically employ a filter subsystem located near the test environment to remove background emissions from a laser delivery fibre and to block Rayleigh scattered laser light from entering a separate fibre that returns the signal to a remote spectrometer (Everall et al., 2002). In this work, fibre lengths of between 2 and 4 cm were used.

2.3. Imprinted polymer

Before imprinting can be commenced it is necessary to add polymer to the optical fibre endface. The epoxy based negative photoresist SU8-2002 (Microchem) was selected for this demonstration because of its liquid state before curing and its chemical and physical robustness after curing. These characteristics make it a permanent addition to the fibre endface once it is properly cured, which is important for the development of stable and repeatable SERS sensors. A drop of this polymer was manually dispensed onto the fibre tip by syringe prior to imprinting.

2.4. Imprinting

Imprinting of the fibre against the h-PDMS mold was conducted by using the precision translation stages of a fibre alignment system (Newport AutoAlign). Both the fibre and mold were loaded onto one stage each, and imprinting was conducted by bringing the coated fibre endface into proximity with the mold so that it was wetted by the SU8, as illustrated in Fig. 2b. Physical contact between the mold and fibre was avoided in order to prevent compression of the flexible mold features. Their proximity was monitored via a CCD camera through appropriate magnifying optics. While in contact with the mold, the SU8 was cured using a three-step process. A 5-min soft bake was first used to heat the SU8 beyond its glass transition temperature, simultaneously dispelling solvents and facilitating pattern transfer. This thermal energy was delivered by convection