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Surface Enhanced Raman Scattering using Metal Modified Microstructured Optical Fibre Substrates

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Abstract *We report the fabrication of metallic metamaterials using microstructured optical fibres as templates. The resulting fibres serve as excellent substrates for surface enhanced Raman spectroscopy and represent an exciting platform for in-fibre plasmonic devices.*

Introduction

Synthesis of metamaterials using micro/nanostructure scaffolds as templates is a powerful means to create 3D structures with appropriate nanometric architecture. Microstructured optical fibres (MOFs) offer versatile engineering of the geometry combining very large surface areas and aspect ratios with outstanding mechanical properties that serve as excellent 3D templates [1]. Here we report the growth of silver granular layers inside the MOF holes by high pressure chemical deposition techniques. The resulting metal-dielectric MOFs serve as exceptional substrates for surface enhance Raman spectroscopy allowing for very long interaction lengths between the fibre's optical guided modes and plasmonic resonances of the silver nanoparticles with benzenethiol molecules used as the analyte.

Materials deposition within MOFs

MOFs are a special class of optical fibres whose guiding properties rely either on modified total internal reflection or on the existence of photonic bandgaps [2]. In MOFs, the aperiodic or periodic arrangement of holes can be tightly controlled during the fabrication process and by choosing an appropriate structure, the spectral and temporal characteristics of light propagating through them can be carefully engineered. A further advancement in the functionalization of MOFs is the inner modification and filling of their capillary holes. The deposition of useful materials inside the fibre's voids has the potential to explore new directions in micro-nanomaterials technology and allow for long interaction length between the fibres guided modes and the infiltrated materials. The incorporation of materials such as polymers, low-melting point metals, and gases has found use in complex optical *in-fibre* devices such as variable attenuators [3], Mach-Zehnder interferometers [4] and Raman scattering gas cells [5]. However the filling of the fibre's capillaries with materials is extremely challenging since their pores have very high aspect ratios, and mass transport throughout their length is restricted. Recently, high pressure chemical deposition techniques have been applied for the inclusion of a wide range of technological important materials within MOF capillaries [1]. By applying the deposition flexibility of high pressure chemistry, the empty pores can be treated as reaction chambers and by flowing a silver organometallic precursor through the fibre we have achieved the deposition of metal granular films along the fibre walls and in this way fashioned a new class of fibre based metal-dielectric metamaterials.

Nanoscale metal-dielectric structures allow for the excitation of surface plasmon (SP) modes which are conduction electron waves at optical frequencies localized along the metal-dielectric interface. SPs lead to high concentration of the electromagnetic fields at the surface boundary and this high localization of the field provides the electromagnetic contribution to surface enhanced Raman scattering (SERS). The ability of metallic nanostructures to mediate SERS effects is essential to achieving high sensitivity Raman spectroscopy. SERS can enhance a Raman signal by more than 10^{14}, making detection practicable with possible applications right down to the single-molecule level [6].

After drawing the optical fibre, heptane is used (in a separate process that is completely independent from fibre fabrication) at high pressure to deliver an Ag-precursor complex into the fibre holes. The high-pressure flow, which can be sustained due to the very high mechanical strength of optical fibres, overcomes mass-transport constraints within the extremely long narrow fibre pores. This is followed by a simple thermal reduction of the precursor, resulting in the annular deposition of Ag nanoparticles inside the holes. The organometallic precursor Ag(hfac)(1,5-COD) (hfac=1,1,1,5,5,5-hexafluoroacetylacetonato, COD = cyclo-octadiene) was used due to its high solubility in heptane, and low decomposition temperature (200°C). In a typical experiment, Ag(hfac)(1,5-COD) is dissolved in HPLC grade n-heptane and the solution is flowed through the optical fibre at 17 MPa by a high performance liquid-chromatography pump. Due to the small volume contained in the fibres, the amount of precursor required for the deposition is very small making the process safe even at the high pressures used in the experiment. The optical fibre is passed through a heating cartridge which is ramped up to 200°C as the precursor flows through the fibre, and in this way initialize the deposition of Ag nanoparticles. As the deposition time increases, the Ag nanoparticles serve as nucleation points allowing the formation of thin layers of silver inside the holes along the heated length. The decomposed ligands are easily removed by the heptane, leaving high purity Ag nanocrystals inside the fibre. Figure 1 shows different Ag coatings achieved by tuning the experimental parameters such as the experimental time, temperature, pressure, precursor concentration and flow rate.

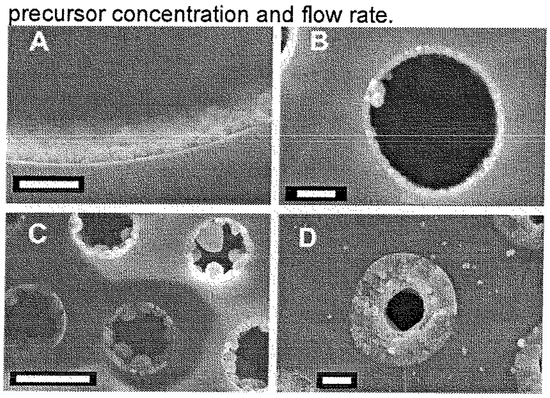

Figure 1. SEM cross section of different MOFs after filling with silver nanoparticles. The coating thickness can be controlled by the experimental parameters. (A) Scale bar is 1 μm. Here, the silver particles are less than 100 nm in diameter. (B) Scale bar is 2 μm (C) Scale bar is 5 μm (D) Scale bar is 3 μm.

SERS characterization

The fibre substrates were tested for SERS activity using benzenethiol as the target molecule. Benzenethiol is a molecule frequently investigated using SERS due to its distinct Raman features and strong affinity for Ag surfaces. All Raman measurements were conducted using a conventional Renishaw Raman spectrometer with a 785nm Ti:sapphire excitation laser. The fibre template used in the SERS characterization consists of 12μm diameter holes in a "honeycomb" MOF configuration with a total of 182 holes.

The sample used in the SERS experiments was a Ag coated MOF approximately 15mm long. The sample was treated with a drop of benzenethiol in ethanol (1mM solution, HPLC-grade). After the drop evaporated, the fibre was rinsed and finally soaked in ethanol for 30 minutes. This procedure ensures that at most a monolayer of the 'dye' was present in the fibres during the Raman measurements.

The incident laser beam was focused onto different areas of the sample as shown in Figure 2a. The Raman photons generated along the fibre are collected in the opposite direction of the incident laser light with the same objective lens used to launch the pump laser into the fibre.

Figure 2b shows the SERS Raman spectra obtained with the Ag MOFs and a control sample with no Ag layer. All the main vibrational modes of the dye molecule can be assigned in the measured data and correspond to those reported in the literature [7]. SERS detection of a monolayer of the dye in the Ag fibre is verified from the absence of the S-H molecular bond of benzenethiol in the SERS spectra, as expected if all the molecules are attached directly to the silver surface [8]. Additionally, no Raman peaks of benzenethiol were observed in the control fibre.

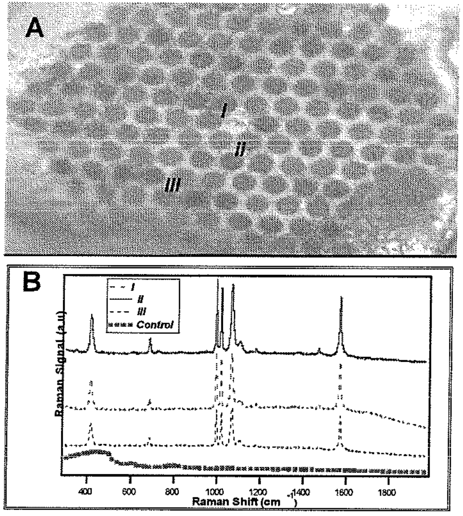

Figure 2. (A) Microscope image of the Ag MOF used in the SERS experiments, indicating the areas where the pump laser was focused. (B) Raman signals obtained with a 20x microscope. The curves are shifted vertically from each other for clarity.

Conclusions

Our technique of depositing silver nanoparticles inside MOFs templates has demonstrated applications in SERS spectroscopy and allows for highly extended photonic/plasmonic interaction inside optical fibres, forming the basis for new classes of *in-fibre* plasmonic devices and sensors.

References

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