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A nanoporous gold membrane for sensing applications

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ABSTRACT

Design and fabrication of three-dimensionally structured, gold membranes containing hexagonally close-packed microcavities with nanopores in the base, are described. Our aim is to create a nanoporous structure with localized enhancement of the fluorescence or Raman scattering at, and in the nanopore when excited with light of approximately 600 nm, with a view to provide sensitive detection of biomolecules. A range of geometries of the nanopore integrated into hexagonally close-packed assemblies of gold micro-cavities was first evaluated theoretically. The optimal size and shape of the nanopore in a single microcavity were then considered to provide the highest localized plasmon enhancement (of fluorescence or Raman scattering) at the very center of the nanopore for a bioanalyte traversing through. The optimized design was established to be a 1200 nm diameter cavity of 600 nm depth with a 50 nm square nanopore with rounded corners in the base. A gold 3D-structured membrane containing these sized microcavities with the integrated nanopore was successfully fabricated and 'proof of concept' Raman scattering experiments are described.

1. Introduction

Biosensors for the direct detection of biomolecules at the single molecule level would be highly desirable for a range of diagnostic applications, especially if these bioanalytes could be delivered sequentially through a nanopore. So far, metallic nanostructures have been shown to provide an enhancement factor of 10^{14} with a large cross-sectional area of 10^{-16} cm^2/molecule using surface enhanced Raman scattering approaches [1]. The rational design of metallic nanostructures for this application, also known as plasmonic substrates or devices, for sensing applications is well established [2]; the functional characteristics of these devices are based upon the behaviour of plasmons at the interface of a metal-dielectric medium. For metallic nanostructures, the electrons in the metal are excited and oscillate within the metal core near the interface with a surrounding dielectric material; these collective electron excitations are known as surface plasmon polaritons.

The potential of nanostructured metallic structures for optical applications has been demonstrated for (i) biosensing applications [3], (ii) surface enhanced Raman spectroscopy (SERS) [4], (iii) guiding and manipulating the light [5], (iv) sub-diffraction limited imaging [6] and (v) trapping of micro/nano-sized particles [7]. In order to apply the nanostructures for these applications, the structure dimensions and geometry have to be appropriate for (i) tuning of the plasmon resonance coupling, (ii) the near field enhancement, (iii) the confinement in sub-wavelength region coupling, (iv) enhanced evanescent waves and (v) the near- and far-field enhancement, [8] respectively to each application. Moreover it is essential that there are high levels of local-electric field intensity at locations within the sensor where the plasmon enhancement of signal from the transducer will be most beneficial — this is especially true for sensing applications where the analyte must be within the region of highest electric field (*E*-field) intensity. Various metallic nanostructures have been proposed for sensing using a range of different shapes and geometries [9], materials [10,11] and fabrication methods [12], notably for the optimization of SERS measurements [13] tip-enhanced Raman scattering, (TERS) [14] and fluorescent enhancement [15]. Most of the nanostructures studied so far are multi-scale nanoparticles and nanocrystals. The nanoparticles can be classified as 1-dimensional [16], 2-dimensional and 3-dimensional nanoparticles i.e., nanorods, nanocrescent and nanopores respectively. More recently planar plasmonic substrates have been developed for 'nanofocusing of plasmons' [17–22] and SERS [23,24].

Although TERS has been applied for the sequence analysis of DNA [25], such a measurement is highly challenging from a practical point of view. Whether nanopores could be designed to yield plasmonic sensors appropriate for the direct detection of single molecules within the pore is a question that still remains. In other words, could the *E*-field be highly confined within the nanopore with a view to providing a sufficiently sensitive nanopore sensor for single molecule detection at translocation?

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Various groups have studied the plasmonic properties of 2-dimensional nanoporous gold films where a change in the pore size provides a shift in the wavelength of the band assign to plasmon resonance [26,27]. Unfortunately, so far, the level of plasmon enhancement is not reproducible which is possibly due to a variation in pore shape and size of the fabricated devices [28–32]. Various teams have studied plasmonic devices based upon the so-called 'bowtie' configuration [31–33]. These structures consist of sharp triangular metallic structures in the shape of a bowtie, where the distance between the two closest triangle tips (the bowtie antennas) can be used to tune the plasmon resonance. Where there is a nano-sized pore located between the bowtie antennas, the localized *E*-field is confined at the pore, in between these antennas [33], yielding a 2D-structured metallic device with an integrated pore. So far the only example of precise 3D-structured metallic substrates with pores have been reported by Lindquist et al., where the 3D nanopore device is a hybrid of metallic pyramid with C-shaped apertures to tailor the plasmonic properties for the application of TERS [29].

In this study we report the design, fabrication and first evaluation results of a 3D-structured nanoporous structure where the *E*-field intensity is highly localized 'at' and 'inside' the pore for sensitive biosensing applications where the analyte is to be passed through the pore.

2. Materials and methods

2.1. Theoretical design of microcavity with integrated nanopore

Fig. 1(b) contains a schematic of the cross-sectional structure used for the theoretical studies. The model consists of a thin layer of water (or air) on which the three-dimensionally structured gold microcavity with a nanopore is placed, in and above the microcavity and the pore. The surrounding medium is also water (or air). As the model in this first instance is a single microcavity, the scattering boundary condition (the scattered field is considered to be fully absorbed at the boundaries of the system, the boundary is transparent to the scattered and the incident *E*-field) is applied outside the structure shown in Fig. 1(b). The cavity radius (R) is varied for the initial studies, and the depth of the cavity (d) is set to R. Several simulation approaches are applied:

Method 1: Three-dimensional hexagonal close-packed microcavities were considered theoretically using the software suite, RSoft DiffractMOD, Synopsis Inc. DiffractMOD employs the Rigorous Coupled Wave Analysis (RCWA) method to obtain the backward diffraction efficiency; periodic boundary conditions are used, as previously described for a different system [34].

In brief, the number of harmonics is set to 5 for the in-plane surface to expand the refractive index and field in Fourier space. The excitation light, which is normal to the opening of the porous membrane, is a plane wave with p-polarized light. The simulations are performed for a wide spectral range (400 nm to 950 nm with 2.5 nm steps), typically with p-polarization. As a figure of merit, the zero order diffraction efficiency (specular reflection) is also obtained. In order to properly establish the *E*-field in and around the drilled square hole, the spatial *E*-averaged power monitor (U_E) given by the Eq. 1 below, is applied:

$$U_E = \frac{1}{2}\int_V \mathrm{Re}[\in(r)]|\mathrm{E}(r)|^2 \mathrm{dV}. \quad (1)$$

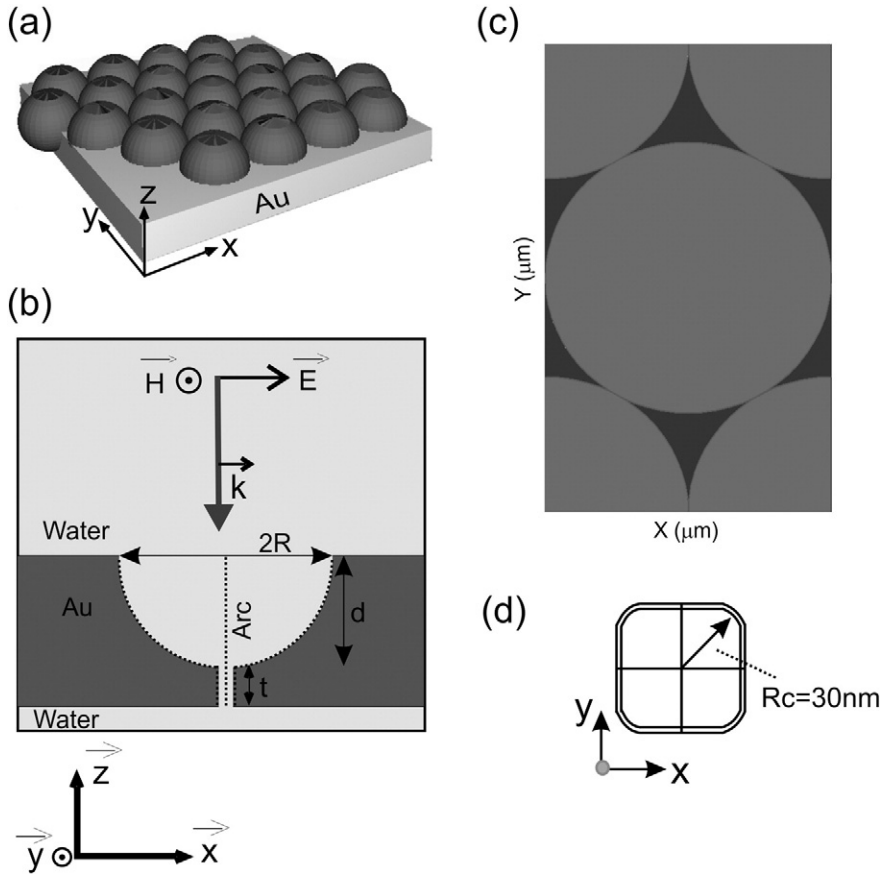

Fig. 1. (a) 3-Dimensional view of the gold nanoporous micro-cavities used for the theoretical simulations in which spheres were arranged in the hexagonal lattice and the height of the sphere immersed in the gold film (grey block) was set to 50% of the diameter of sphere. The background medium was defined as water or air. (b) 2-Dimensional cross-sectional view of the nanoporous microcavity plus the incoming EM field (The dotted line labelled arc is used for ascending plots of *E*-field intensity as described in the text.) (c) The top view (XY-plane) of the gold membrane which shows a single unit cell of the hexagonal lattice (1200 nm diameter micro-cavity). (d) The top view of the pore upper cross section where R_c is defined as the radius from the centre of the square pore.