Nanogap Ring Antennae as Plasmon Coupled, Dichroic SERRS Substrates for Biosensing

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We explore the use of engineered nano-gap plasmonic ring systems in biosensing. By employing cutting edge nanofabrication methods we seek to exploit the extraordinary optical properties of metallic nanostructures in a range of novel ways targeted toward extremely sensitive molecular detection.

Surface enhanced (resonance) Raman spectroscopy (SE(R)RS) is a powerful sensing tool which relies on molecular interaction with the fluctuating plasmon field of a resonating nanoparticle. Using this method it has been shown that SERRS can rival the sensitivity of fluorescence techniques, enabling single molecule detection and characterisation.[1] As nanoengineering techniques have become more advanced in recent years there has been a move toward fabricating ever more complex nanoparticle geometries, with the aim of creating functional, tunable sensing substrates with a uniform distribution of intense localised plasmon fields.

In this work, we explore the use of nano metallic split-ring antenna as powerful, multifunctional biosensors with dichroic optical properties. Fabrication via electron-beam lithography allows for the strict control over structural geometry that is necessary to accurately tune the ring's multiple, polarisation dependant plasmon resonances to particular wavelengths.[2] In doing so, we demonstrate that we can tune their optical response such that they exhibit two independently addressable high frequency plasmon resonance modes, each tuned to the absorption wavelength of a differently coloured Raman reporter molecule and its corresponding laser excitation wavelength (Figure 1).[3, 4] This allows the single geometry ring structures to act as tailored SERRS sensors for low concentration DNA analyses at two distinct wavelengths.[4]

We go on to report on the fabrication, optical characterisation and application of a new generation of ultra-small multiple-split nanoring antenna.[5, 6] Using electron-beam lithography, splits of ca. 6 nm are engineered into silver nanophotonic ring structures to create concentrated areas of localised field coupling, which can be exploited for enhanced plasmonic applications. We compare the plasmonic properties of three devices, containing 3, 4 and 5 splits respectively, which have been spectrally tuned to 532 nm. Using finite element analysis, we explore the distinct plasmonic characteristics of each structure, and describe how variations in surface charge distribution effect inter-segmental coupling at different polarisation angles (Figure 2). The impact these changes have on the sensory functionality of each device was determined by a competitive DNA hybridisation assay measured using surface enhanced resonance Raman spectroscopy. The geometry of these novel, circular, multiple-split rings leads to unique plasmon hybridization between the numerous segments of a single structure; a phenomena we demonstrate is applicable to extreme Raman sensitivity, and may also find use in metamaterial applications.

References

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Figures

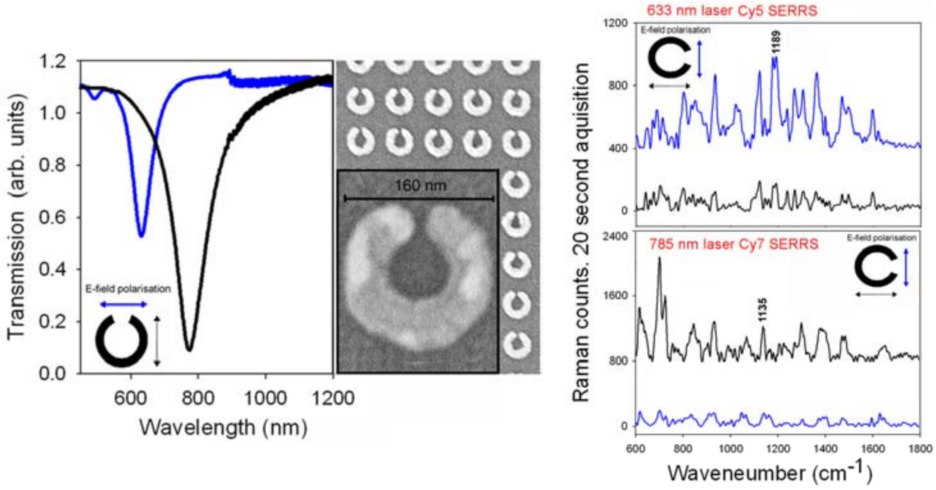

***Figure 1. Left** – SEM and transmission spectra of an 80 nm radius Ag split-ring resonator sensor array with 2^{nd} and 3^{rd} order resonances tuned to 785 and 633 nm respectively. **Right** –SERRS from an identical array modified with a 1:1 ratio of Cy5 and Cy7 labelled oligonucleotide sequences hybridized to complimentary strands attached to the sensor surface. Measurements were performed at 633 and 785 nm and data was collected when the electric field vector of each laser was orientated both parallel and perpendicular to the split in the ring geometry.*

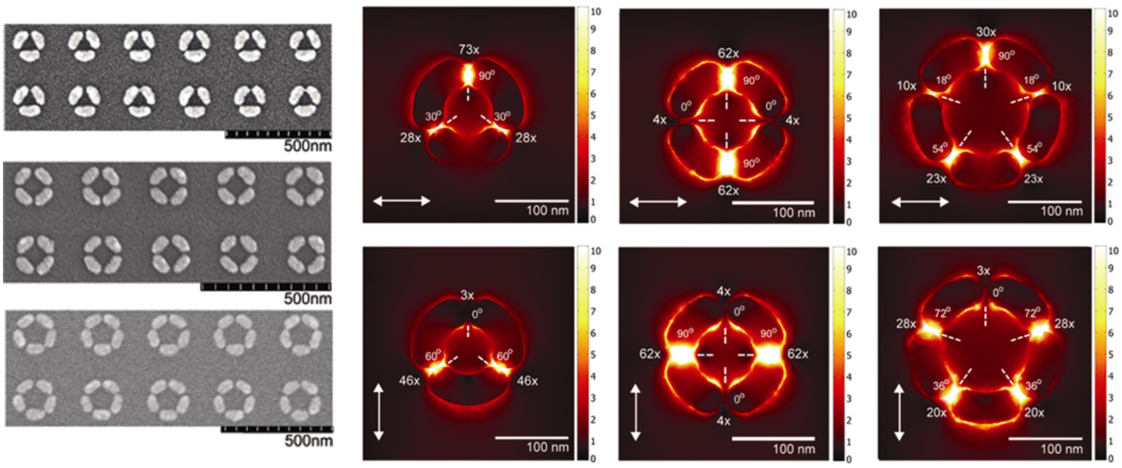

***Figure 2. Left** – SEM of multiple-split nanoring antenna with average gap sizes of 6nm or less. **Right** – Finite element analysis of the plasmonic field distribution around each structure at resonance.*