Array of silver nanocylinders: plasmonic properties, the effects of a close silver layer and fluorescence enhancement

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Abstract

Surface-enhanced spectroscopy is a branch of techniques that enhance light emission from molecules at nanoscale proximity to plasmonic structures. Examples of SES include surface-enhanced fluorescence (SEF), surface-enhanced phosphorescence, surface-enhanced Raman spectroscopy (SERS), surface-enhanced infrared absorption and surface-enhanced chemiluminescence. We are interested in applying plasmonic structures for enhancing fluorescence signals, what may be very important for detection of low amounts of analytes in diagnosis of infectious diseases and cancer cells; and in monitoring of healthy, food and environment.

Different geometries were already applied to SEF. The one that produced the highest enhancement in average (not in hot spots) was an annealed thin silver layer over a silver mirror, with an enhancement factor of 208 [1]. We studied bi-dimensional periodic arrays of silver single and double nanocylinders with 30-80 nm of diameter, and the effects of an underlying 45-nm silver layer, as such a layer can lead to higher optical signals [2].

The experimental structures were constructed by electron-beam lithography in conjunction with thermal evaporation and atomic layer deposition. 20- (set 1) or 40-nm (set 2) high cylinders and double cylinders (dimers) with 30 to 80 nm of diameter were fabricated on top of fused silica in structures without mirror. With mirror, firstly a 45-nm silver layer was deposited and covered by a 15-nm-thick separation alumina layer. Then, cylinders were constructed on top of it, and another 15-nm alumina layer was deposited for protection against oxidation and for mechanical stability [2]. The period was defined as 150 nm in both directions of the array.

Similar structures were simulated by finite element method (FEM) using COMSOL Multiphysics 3.5 a (see Figure 1A), with variations of diverse parameters. The excitation was defined as a TEM (transverse electromagnetic mode) planar wave from the top. The materials were defined by their refractive indices, being silver modeled by the tabulated values of Lynch and Hunter [3].

We analysed the optical properties and the tunability of the surface plasmon resonances of the geometries by performing simulations, and compared simulated attenuance spectra with the ones obtained by transmission measurements. We also evaluated the enhancement of the second power of the electric field ($|E|^2$) averaged over these structures for a first analysis of fluorescence enhancement: $fluorescence\ intensity \propto |E^2|QY$, with the quantum yield $QY = \frac{\Gamma}{\Gamma + k}$, where Γ is the radiative decay rate and k is the non-radiative decay rate [4]. Finally, we spin coated 55-60 nm layers of polyvinyl alcohol (PVA) with embedded fluorochromes in order to perform fluorescence experiments on these structures. Qualitative measurements were obtained by using a confocal microscope. The fluorochromes we used were Fluorescein, excited at 488 nm, and Alizarin Red S, excited at 514 nm. Their quantum yields are almost unitary or almost zero, respectively.

Figure 1B shows examples of attenuance for structures with an underlying thin silver layer. There are two strong resonances at 460 nm and at 500-620 nm, and a not clear resonance or mixed modes around 400 nm. Theoretical calculations show that the periodic structures can produce a Bragg vector that can excite propagating surface plasmons (PSPs) at 403 nm. The other red shifted peaks are due to quadrupolar (460 nm) and dipolar (500-620 nm) localized surface plasmon (LSP) resonances at the nanocylinders. The LSPs can be tuned by varying controllable parameters, such as: alumina separation layer thickness, thickness of the cap layer, cylinder diameter and the refractive index of the cover layer (alumina for the constructed structures). Because of the latter tuning parameter, the structure can be applied to surface plasmon resonance sensing based on wavelength interrogation. The tuning can be approximated by linear equations for each parameter. An enhanced transmission at long wavelengths was observed when cylinders were placed over the thin silver layer (negative normalized extinctions in Figure 1B). The reason is not established, but we know it is not due to PSPs.

The $|E|^2$ over the top of the structure is enhanced due to the near field. Compared to a dielectric substrate, enhancement of up to 21.8 times was achieved by dimers in longitudinal polarisation, being the mirror responsible for a factor up to 5.6 times.

In most cases, Alizarin Red S had higher enhancements than Fluorescein, what can be explained by the very low quantum yield [5], which allows an extra enhancement. Nevertheless, the maximum enhancement was acquired for Fluorescein on a mirror without cylinders, 30.8 times. This enhancement on a 55 to 60-nm layer was higher than the calculated enhancement of $|E|^2$ just at the top surface (4.2 times). However the quantum yield of Fluorescein is almost unitary, modification in the radiative transition rate must have played an important role, as it can lead to a brighter fluorescence during a shorter time. The highest enhancement with cylinders was obtained for Alizarin Red S with a granular mirror (fabrication defect in set 1), 24.2 times.

References

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Figures

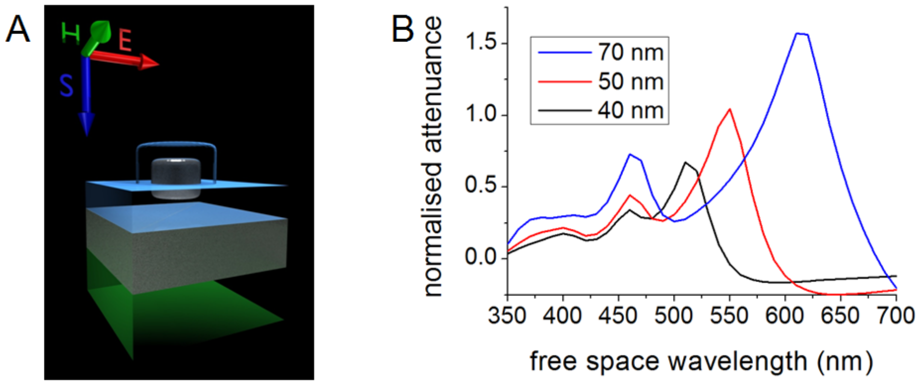

Figure 1. A) Single cell of a periodic array with single cylinder and silver layer. Materials: silver (grey), alumina (blue) and fused silica (green). **B)** Example of normalized attenuance (reference subtracted) for structures with an underlying silver layer.

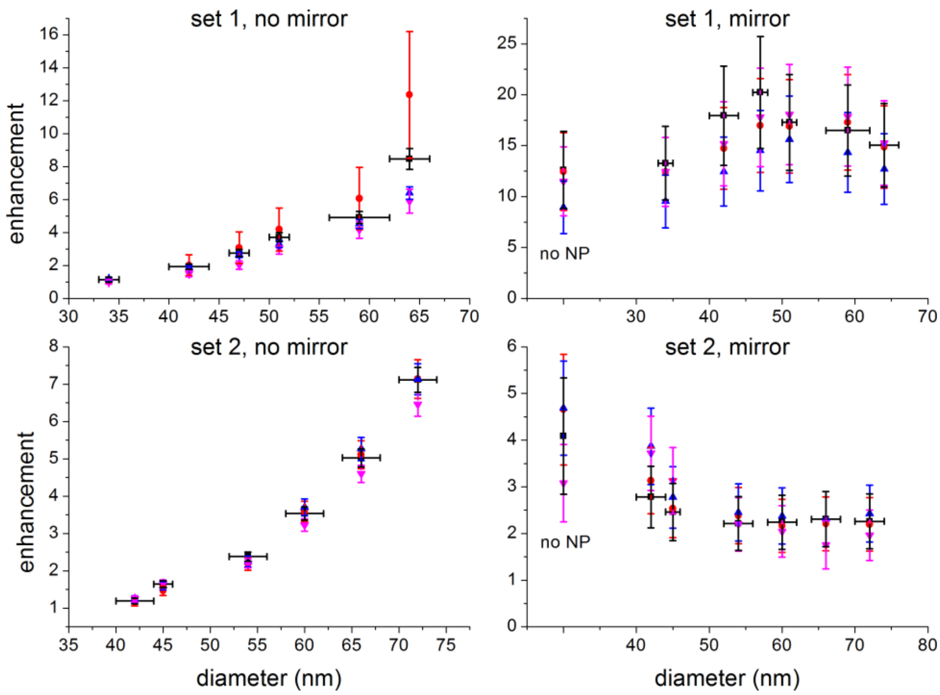

Figure 2. Example of fluorescence enhancement: Alizarin Red S on single cylinders. The silver layer of set 1 presented granularity.