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# Optimal geometric parameters of ordered arrays of nanoprisms for enhanced sensitivity in localized plasmon based sensors

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ABSTRACT

Plasmonic sensors based on ordered arrays of nanoprisms are optimized in terms of their geometric parameters like size, height, aspect ratio for Au, Ag or $Au_{0.5}$–$Ag_{0.5}$ alloy to be used in the visible or near IR spectral range. The two figures of merit used for the optimization are the bulk and the surface sensitivity: the first is important for optimizing the sensing to large volume analytes whereas the latter is more important when dealing with small bio-molecules immobilized in close proximity to the nanoparticle surface. A comparison is made between experimentally obtained nanoprisms arrays and simulated ones by using Finite Elements Methods (FEM) techniques.



## 1. Introduction

Biosensing emerged in the past decade as one of the most interesting fields of application in plasmonics (Anker et al., 2008; Brolo, 2012; Schuller et al., 2010; Stewart et al., 2008; Yu et al., 2013). Among different approaches, optical sensors based on the Localized Surface Plasmon Resonance (LSPR) have been demonstrated to have huge sensitivity to even extremely small changes in the refractive index of the medium (Brigo et al., 2014; McFarland and Van Duyne, 2003), as well as to very thin layers of bio-molecules. Indeed, the shape and position of the resonance is strongly dependent on the dielectric properties of the local surrounding medium (Beeram and Zamborini, 2011; Malinsky et al., 2001; Mock et al., 2003). This gives a powerful tool to detect small changes in the refractive index, due to the presence of an analyte, exploited in a number of nanostructures configurations, from single colloidal particles to ordered arrays of nanoparticles (Anker et al., 2008; Chan et al., 2010; Dondapati et al., 2010; Haes and Van Duyne, 2002; Haes et al., 2005; Itoh et al., 2004; Jain et al., 2008). Geometric details of the nanostructures (made by isolated or interacting building blocks or monomers) have been demonstrated to play an important role in the formation of plasmons. In particular, monomer size (Chen et al., 2009, 2008; Joshi et al., 2012; Mayer and Hafner, 2011; Slaughter et al., 2011, 2010), shape (Becker et al., 2010; Bukasov et al., 2010; Busbee et al., 2003; Chen et al., 2008; Lee et al., 2009; Marinakos et al., 2007; Millstone et al., 2005; Nehl et al., 2006; Wei et al., 2010) and mutual interaction (Guo et al., 2011; Jain et al., 2007; Reinhard et al., 2005; Sonnichsen & Alivisatos, 2005; Wang & Reinhard, 2009) can be tuned to control field enhancement and confinement.

Among various configurations, those involving the presence of 2D ordered arrays of nanostructured building blocks are particularly appealing for their possibility of fine tuning the resonance position through a control of the lateral interaction among the building blocks. Traditional top-down synthesis techniques (EBL, FIB, etc.) are still quite expensive, and even if coupled to pattern reproduction techniques (like nanoimprint lithography, NIL), they can yield only few $mm^2$ of active areas. Since the seminal work by Van Duyne's group on Nano Sphere Lithography (NSL) (Haynes and Van Duyne, 2001; Hulteen et al., 1999; Jensen et al., 2000), cheap, wide area, ordered array LSPR biosensors can be fabricated exploiting self-assembly strategies to produce 2D ordered plasmonic nanoprism arrays (NPAs) on several $cm^2$ active areas. Moreover, some of the most important geometric properties of the nanostructures can be conveniently controlled by acting on a few experimental parameters in the fabrication process.

When designing a (bio)sensor the fundamental parameter to be optimized is its sensitivity. In general, a systematic investigation of this parameter for LSPR detection scheme can be easily done in semi-analytical form only for simple geometries like isolated

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spherical or spheroidal nanoparticles, for which analytical solutions (e.g., Mie or Gans theory) can be used to quickly model the influence of the sensor geometric and dielectric parameters on the sensitivity (Piliarik et al., 2011). Such theoretical analysis is much more demanding for less symmetric topologies or shapes like for instance the nanoprism one (either isolated or in an interacting configuration like for NPA) despite the large number of experimental papers dealing with plasmonic sensors based on this kind of interacting monomers (Willets and Van Duyne, 2007). Several attempts of optimization (even if not so systematic) of the NPA geometry have been so far described in literature: they mainly focused on the variation of geometric parameters, in particular height and base side (Haynes and Van Duyne, 2001; Yonzon et al., 2004), on the effect of thermal annealing (Haes et al., 2004) or on the chemical modifications to the metal surface (Malinsky et al., 2001). From a different point of view, also an optimization has been attempted for achieving the best chemical coupling between analytes and the sensors (Zhao et al., 2007, 2006) or to use peculiar features of the analytes (e.g., characteristic resonances) to further enhance the sensitivity (Zhao et al., 2008). All these works give a general framework on how a sensor can be optimized: in general, the main phenomenon triggering the sensitivity of a sensor is the interaction between the analyte and the confined electromagnetic field generated by the plasmon, which, in turn, is excited by the external illumination. Therefore, the sensitivity can be enhanced by tailoring the plasmon electric field distribution in such a way that the interaction with the analyte is maximized. Another important feature is the good coupling to the far-field, since both illumination and detection take place on the far-field plane waves. Although much work has been done, a systematical investigation is not present.

Therefore, the aim of the present paper is the investigation and optimization of the sensitivity of this kind sensors with respect to monomer composition, size, aspect ratio by combining computational methods based on Finite Elements Methods (FEM) modeling and experiments with nanoprisms arrays (NPAs) synthesized by NSL. In particular, we used FEM in the frequency domain. Differently from exact techniques, like the Mie theory, Generalized Multiparticle Mie theory or Green's function approach, which rely on the presence of particular symmetries (typically, spherical symmetries), Finite Elements can model complex, arbitrarily shaped nanostructures. This makes it possible to give nanostructures the correct shape (deduced from experimental measurements), and also consider the effect of substrates (most important for supported nanoparticles) and model different kind of analytes, from homogeneous refractive index media to thin layers of molecules.

## 2. Material and methods

### 2.1. Experimental

Gold and Silver nanoprism arrays (NPAs) have been fabricated by NanoSphere Lithography (NSL, a colloidal patterning procedure), followed by film deposition. The samples have then been structurally characterized by AFM and FEG-SEM and optically by linear absorption. The sensitivity measurements have been carried out both by varying the refractive index of the environment and by depositing silica layers with increasing thickness, to mimic the local dielectric effect of an analyte layer.

### 2.2. Materials

All the chemical reagents were purchased from Sigma-Aldrich. A 10 wt% solution in water of monodisperse ($D=496\pm5$ nm) polystyrene nanospheres (PS NS) from Microparticles GmbH has been diluted in a 50/50 solution of isopropyl alcohol to lower the surface tension. Conveniently cut soda-lime glasses were used as substrates. Glass cleaning was performed by an acidic piranha solution (98% $H_2SO_4$+35% $H_2O_2$, 7:3) at 90 °C for 60 min, followed by a basic piranha (25% $NH_4OH$+35% $H_2O_2$, 3:1) at 80 °C for 10 min. Glasses were then conserved in ultrapure water before their use.

### 2.3. Sensors fabrication and characterization

The nanofabrication of the sensors has been obtained by the NSL technique (Brigo et al., 2014; Haynes and Van Duyne, 2001; Hulteen et al., 1999; Jensen et al., 2000). Briefly, a few drops of solution containing PS NS are placed on a piranha-cleaned glass, which is then carefully immersed in water in a crystallizing glass vessel. As a result, a monolayer (ML) of nanospheres is formed on top of the water, the spheres being organized in a close-packed configuration. Another glass is then used to carefully pick up the monolayer and let dry in air for half an hour. This procedure yields large areas (of the order of some $cm^2$) of patterned substrate. The typical area of the ordered domains of the 2D crystalline ML extends up to several hundreds of $\mu m^2$.

After ML formation, to get the plasmonic nanoarray, a deposition of gold or silver is performed by orthogonal thermal evaporation up to the desired height (typical values in present work are 50–60 nm). After the deposition, a simple adhesive tape stripping removes the nanospheres together with the residual metal upon them. The result is an ordered array of nanoprisms (NPA) arranged in a honeycomb lattice.

Structural characterizations were performed by scanning electron microscopy on a Gemini Leo 1530 SEM microscope and by atomic force microscopy on a NT-MDT Nova PRO-Solver AFM microscope. The optical properties (absorbance/transmittance) of the sample were measured both with a Jasco V-670 spectrophotometer and with an Ocean Optics setup with a DH-2000-BAL source coupled to HR4000CG-UV–NIR spectrometer. Ellipsometry has been performed using a J. Woolham V-VASE Spectroscopic Ellipsometer.

### 2.4. Sensivity measurements

For the measurement of the bulk sensitivity, $S$, the samples have been immersed into three solutions with different refractive index (ultrapure water, $n=1.33$; ethanol, $n=1.36$ and glycerol, $n=1.47$).

For the measurement of the surface sensitivity, $S_0$ i.e., the sensitivity to few-nm thick layers around the NPA, incremental thin layers of silica have been deposited by RF-magnetron sputtering on the NPAs and transmittance spectra have been acquired. At each step, the thickness of the deposited $SiO_2$ layers was measured both by AFM and by ellipsometry as a check. The sputtered silica refractive index was determined by ellipsometry measurements as well.

### 2.5. FEM simulations

Simulations have been carried out using a commercial software for Finite Elements Method (FEM) (Brigo et al., 2014, 2012; Jin and Jin, 2002), COMSOL Multiphysics version 4.3a. Nanoprisms array is modeled by considering the unit cell (containing 2 prisms), as shown in Fig. 1a, and inserting periodic boundary conditions in the array $xy$ plane. In the $z$ direction, orthogonal to the prisms plane, the substrate is modeled as semi-infinite; the nanoprisms are placed directly onto the substrate. The functionalization layer is conformal to the prisms, and has variable thickness. Over the