Flexible plasmonic and strain sensors: fabrication, design and perspectives

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Abstract. In this paper, we aim at debating the perspectives for plasmonic strain sensors which have attracted interest for the past five years. In particular, we strive to discuss the choice of strategy to increase the sensitivity, either by developing random or ordered assemblies of metallic nanomaterials.

1. Introduction

For the past twenty years, nano-optics has emerged as a promising research field thanks to huge progress in nanofabrication and offers great technological potential for applications in fields such as biology, medicine or chemistry. One topic of particular interest during the last decade has been the concept of coupling. In particular, the coupling between plasmonic nanoparticles and films is of prime interest and shows a great technological potential to design perfect black absorbers as well as highly-sensitive biosensors [1]. However, another type of coupling has started to attract the attention of the nano-optics community. Indeed, since the establishment of the well-known “plasmon ruler equation” by El-sayed and coworkers [2-4], the number of numerical and experimental studies about the coupling between two nanoparticles –whether homo- or hetero- dimers- exploded [5-10]. The interest for
plasmonic coupling between metallic NPs has also been extended to assemblies of nanoparticles whether random [11-13] or well-ordered [14]. If the plasmon ruler equation allows predicting that the redshift $\Delta \lambda$ in the Localized Surface Plasmon Resonance (LSPR) wavelength of the metallic NP dimer longitudinal dipolar mode almost exponentially increases with decreasing interparticle separation distances [2-4], other groups including ours showed through experimental [8,11,13] as well as numerical studies [15,16] that for ultra-small interparticle separation distances- that is to say few nanometers- a second mode at lower wavelength can appear due to the coupling between multipolar modes of the metallic NPs.

Within this scientific context, different groups have started investigating the development of plasmonic strain sensors. The first prototype of plasmonic strain sensors was thus proposed by Liz-Marzan and coworkers in 2007 [17]. It was made of Au NPs deposited onto an elastomeric film. Its principle is based on the decrease of incident light absorption when the composite film is stretched and the number of enlightened metallic NPs thus decreases. Therefore, this first prototype was not color-changing but absorbance-changing based. Later, a team from the ETH Zürich has shown that the inter-NP coupling changes of densely-packed 2D Au NPs layers induced by mechanical deformation of the elastomer film embedding the NPs may lead to color changes. This study paved the way for developing plasmonic 2D strain mapping using polarized incident light [18]. Another way of conceiving such strain sensors may consist in monitoring the plasmonic coupling apparition along the transverse direction to the tensile direction. This proof-of-concept [19] has been brought by Thomas Bürgi’s group.

In this paper, we propose to give new insights about the fabrication and design of plasmonic strain sensors based on our more recent research developments.

2. Random assemblies of nanostructures

The sensitivity of plasmonic strain sensors strongly depends on ratio between the diameter of the NPs and the inter-NP distance distribution. The sensitivity of these prototypes is therefore limited by the small size of colloids since the displacement of the metallic NPs is proportional to the centre-to-centre distance between the metallic NPs. This may explain why it may be mandatory to stretch strongly prototypes made with colloids before color-changes apparition [16,19]. Therefore, an alternative for designing strain sensors made with random metallic structures may come from a higher degree of complexity in the structures which are fabricated. For instance, nanorods which are vertically grown onto PDMS (polydimethylsiloxane ) but somehow tilted to the normal direction to the surface offers good promises (see Figure 1). Numerical simulations have already shown the high potential of such a system [20]. This potential lies in the possibility to excite coupled longitudinal plasmon modes along the long-axis of the nanorods when the incident light polarization is in the same azimuthal direction as the long axis. Indeed, such coupled modes are much more sensitive that transverse plasmon modes and experimental investigations reveal sensitivity to strains as high as 2% which is among the highest values in the literature for the moment [21].

Figure 1: (left) Scheme of the random Au assembly of nanorods, (right) variation of the resonance wavelength of the coupled longitudinal plasmon mode of the rods as a function of the
3. **Ordered assemblies of nanostructures**

In this section, we discuss several configurations with ordered NPs made on ductile polymeric substrate such as PET (polyethylene terephthalate). For instance, one of them is linear chains of Au NPs which are 200nm large and 50nm thick and exhibit an initial gap of 5nm (see Figure 2). Optical extinction performed on such systems with incident light polarization along the chain direction allows inducing coupling between Localized Surface Plasmon Resonances of the metallic NPs. As shown on Figure 2d, the LSPR wavelength is 688nm for the initial 5nm gap and shifts to 720nm for 50nm gap either 9% of deformation of the substrate and to 760nm for 100nm gap either 20% of substrate deformations. Therefore the strain sensitivity $\delta \lambda$ amounts to 3.6nm per 1% in substrate deformation which is among the highest values ever reported. Other geometries have also been investigated and deserve attention.

Figure 2: (a) Chain of 200nm nanodisks with an initial gap of 5nm (no deformation) led on a PET substrate, (b) similar chain with a gap of 50nm (deformation of 9%), (c) similar chain with a gap of 100nm (deformation of 20%), (d) optical extinction spectra for such systems with incident light polarization along the chain direction. The coupling can be observed by a strong redshift of the plasmon resonance.

4. **Conclusion**

In this paper, it has been shown that ordered arrays of metallic NPs may exhibit larger strain sensitivity than random arrays of self-assembled nanostructures, especially due to their larger diameter/size. However, self-assembled nanostructures present two main advantages: i) the possibility to achieve high density of substrate coverage and ii) the isotropy of the optical properties which is of prime interest for strain sensors probing deformations whose main direction is not known in advance. Recently, it has been demonstrated that it was achievable to map strains at the nanoscale by monitoring NP displacements [22-24]. The next step is probably to achieve such strain mapping by optical tools. Finally, this paper was the occasion to pinpoint the key questions and scientific barriers which still have to be removed in order to develop such a technology.
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