Mechanoplasmonics and perspectives of applications for flexible plasmonics

A joint PhD delivered by the University of Technology of Troyes, France, and the Eberhard Karls University of Tübingen, Germany

Supervisors : Prof. Thomas Maurer (UTT) and Prof. Monika Fleischer (Univ. Tübingen)

For the past twenty years, microelectronics companies have implemented the *4R principle*: *Reduce, Reuse, Recycle* and *Recreate*. This is how **nanotechnologies** may appear as a promising way to improve materials properties as well as to integrate new functionalities into matter with **reduced quantities of matter**.

In this context, a scientific key question remains the **mechanical robustness of nanoparticles (NPs)** integrated into components. One aspect of this robustness is **the possible modification of NP functional properties due to their deformations and/or to their displacements** when the substrate undergoes mechanical strains. In the framework of this project, we will focus on plasmonic NPs, which are noble metal (gold, silver) NPs that interact strongly with light. By comparing experimental and numerical approaches the project will look for evidence how optical properties of metallic NPs may be mechanically tuned by applying mechanical strains to the substrate which supports them. Recently, a hot topic in plasmonics has been the development of active plasmonics which gives the possibility to actively control plasmonic properties of metallic NPs by applying an external field (electric, magnetic, thermal,…), but little has yet been done about combining plasmonics and mechanics. This requires in particular removing technical barriers about the fabrication of metallic NP arrays onto elastomeric substrates and instrumental barriers to perform optical measurements with applied strains.

The aim of this project is to further develop such mechanically tunable systems in order to **use metallic NPs as nanogauges in order to monitor materials strains at the sub-microscale and/or nanoscale**. This is of high interest for integrating strain sensors into microelectronic components but also to obtain a better understanding of mechanical material properties by leading a multi-scale analysis, monitoring NP deformation and/or displacements at the sub-microscale taking advantage of Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) or optical microscopy/ spectroscopy.

To answer the scientific questions above, the **major technological objective** of the project will consist in developing **strain nanosensors**. Two main strategies will be followed:

1. **The fabrication of colour-changing materials** based on the displacements and/or deformations of metallic NPs. What is aimed for is the increase of the colour-changing sensitivity depending on the applied strains, which requires advances in the design of such nanocomposites (see Fig. 1a)
2. **The integration into matter of metallic nanogauges** whose displacements may be optically monitored using an optical fiber or a microscope (see Fig 1b).

For both demonstrators, strains can be easily quantified using optical fibers and/or portable spectrometers in order to monitor spectral shifts of the plasmon resonances or to image and monitor displacements of the pixels. **A major asset remains the possibility to easily obtain access to strain directions using polarized incident light.**

Such technologies could remove a technological barrier for industries who need to monitor:

- **Large strains** (>1%)
- With **contactless sensors**, that is to say without wires connected to an acquisition system
- Or at micro- or nanoscale like for microelectronics
- **Without any adhesion layer** (compared to all commercial strain sensors)
- And with an easy-to-read system.

(a) (b)

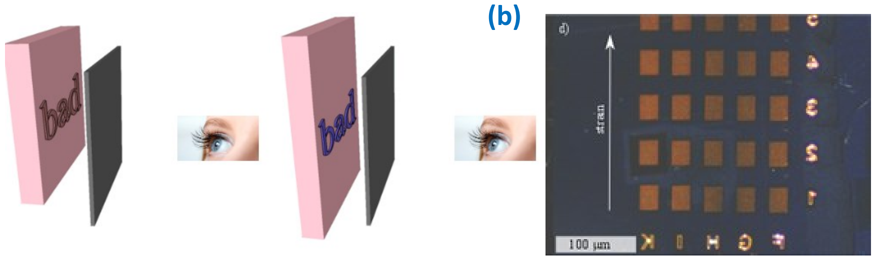

Figure 1: (a) A plasmonic strain sensor prototype using a polarizer film (in grey) where the word "bad" is polarized along the vertical direction and where there is no preferential polarization outside the word "bad". (Left) In the absence of strains, there is no coupling and using the polarizer film, the plasmonic strain sensor exhibits a homogeneous color. The word "bad" cannot be distinguished. (Right) When the plasmonic strain sensor has been elongated (along the horizontal direction), the plasmonic coupling appears along the vertical direction and through the polarizer, the word "bad" can be easily distinguished due to its color-change. (b) Optical microscope image of nanogauges deposited onto PDMS (polydimethylsiloxane). The image was taken after 25% strain was applied to the substrate with square arrays of NPs.

Therefore, the PhD student will acquire both experimental and numerical skills which are highly demanded both in academic and industrial research. As a matter of fact, the deposition of metallic nanostructures onto flexible substrates is a real technological breakthrough which requires various expertise in nanofabrication. Thus, the candidate will develop many skills in **nanofabrication**. Indeed, the project will focus on the combination of top-down techniques, among them electron-beam lithography (EBL) and nanoimprint, and of bottom-up routes, among them colloidal synthesis and evaporation-driven self-organization, which are at the state-of-the-art of nanofabrication. In Tübingen, the PhD student will mainly focus on the direct transfer of NP dimers onto elastomeric substrates while in Troyes, he/she will prepare a PDMS stamp with arrays of holes and then deposit metallic NPs inside the holes via the evaporation-driven self-organization technique offered by the Smartforce® technology which has been acquired in 2018 by the Nanomat' platform (see Figure 2).

(a) (b)

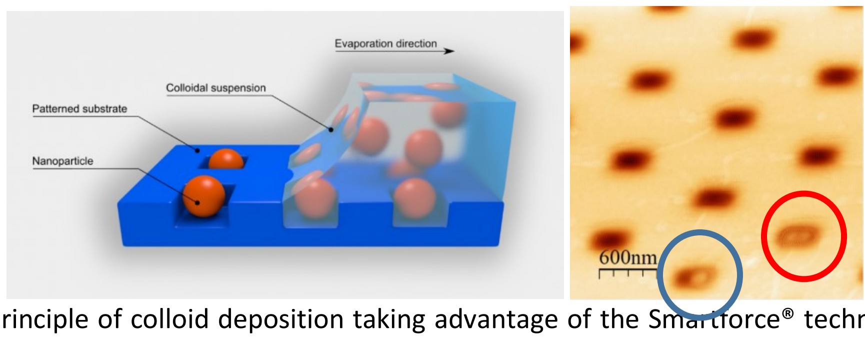

Figure 2: (a) Principle of colloid deposition taking advantage of the Smartforce® technology. Printed with the permission of Smart Force Technologies. (b) AFM image of a PDMS stamps with holes which were prepared by our team. In the red circle, a dimer of NPs can be seen which has been deposited into the hole, while in the blue circle, there is only one NP in the hole. All the other holes are empty. This sample was prepared without Smatrtforce®. The Smartforce technology should help us to fill all the holes with NP dimers.

The PhD student will also acquire solid knowledge and expertise in both mechanics and optics. Once the nanostructures are fabricated onto the substrates, **the project will advance the state-of-the-art in mechanics in two aspects** :

1. **The characterization of the substrate strains at the nanoscale** by monitoring NP displacements
2. **The deformations of the NPs themselves** when the substrate suffers mechanical and/or thermal strains.

Concerning the originality from the plasmonic side, **the main ambition of the project will be to take advantage of in-situ mechanical and optical tests to probe near-field coupling for gaps in the *sub-10nm* range**. Indeed, by stretching elastomeric substrates in the transverse direction to the NP dimer axis, it should become achievable to investigate gaps in the *sub-10nm* range (see Figure 3). If the long axis of the dimer is perpendicular to the stretching direction, the necking of the flexible substrate leads to a decrease in the gap size (see **Figure 3**). This will make it possible to decrease the gap size to below the limit of the lithography setup. In order to obtain sufficient optical resolution, it is necessary to investigate sufficiently large nanostructures (100-200 nm) with gaps as small as possible taking advantage of EBL (10-20 nm). **The objective of the project from the plasmonic side** will be to **investigate the impact of nanostructure deformations on their optical properties.** To complete this goal, attention will be focused on **nanostructures such as cylinders, crosses or nanorings to monitor the influence of their mechanical deformation,** and on **dimers for the gap investigations.**

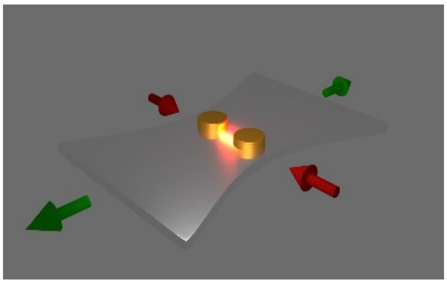

Figure 3: Description of the optical measurements with applied strains to the elastomeric substrate in order to investigate variations in the plasmonic coupling.