3-year PhD position

Functionnalized metallic nanostructures embedded in dielectrics for Surface Enhanced Raman signals

funded by Nantes University and Labex Interactifs (http://labex-interactifs.pprime.fr/)

Application opens from: March 2021

Starting date: between September and December 2021

Collaboration between :

Institut Pprime, CNRS-Univ. Poitiers**,** UPR 3346, Dpt de Physique et Mécanique des Matériaux,

SP2MI, 11 Bld Marie et Pierre Curie, 86360 Futuroscope Chasseneuil du Poitou, France

And

Institut des Matériaux Jean Rouxel (IMN), CNRS-Univ. Nantes UMR 6502,

BP 32229, 2 rue de la Houssinière, 44322 Nantes Cedex 3, FRANCE

Subject

Chemical sensors have become an indispensable part of our technology-driven society and can be found in various fields such as chemical process, pharmaceutical, environmental, security and industrial safety applications to highlight a few of them. Liquid or gas sensors based on Raman spectroscopy are used nowadays in several industrial processes. However, the weak efficiency of the Raman process limits its use as an analytical technique to high concentration measurements. This drawback can be overcome with the use of plasmonic nanoparticles that present localized near field amplifying regions, called hot spots, due to Surface Plasmon Resonance (SPR). Furthermore, a dielectric capping-layer of controlled thickness (in the order of a few nm) would protect the metallic nanoparticles from external aggressions while preventing selective adsorption and direct interaction between the nanoparticles and the probed molecules. Moreover, the chemically inert capping-layer could also enable the sensor substrate to be functionalized or grafted, but also to be cleaned and reused thus ensuring long operational lifetime, reproducibility and durability.

The PhD student will contribute to the **FUNSERS project** (funded by Labex Interactifs) that aims at the development of such novel sensitive SERS (Surface Enhanced Raman Spectroscopy) substrates consisting of large-scale 2D periodic arrays of strongly coupled metal nanoparticles sandwiched between dielectric layers so as to obtain surfaces with extremely high-density of hot spots. The project addresses different scientific issues concerning 1) the production of nanostructured and functionalized surfaces, 2) the wavelength-dependent plasmonic near-field enhancement, and 3) the plasmon/molecules interactions for reproducible sensing applications. It takes the advantages of the complementary expertise and facilities available at Institut Pprime (PPNa team) at Poitiers and Institut des Matériaux Jean Rouxel (IMN) at Nantes.

The original knowhow developed within Institut Pprime consists in producing plasmonic nanoparticle arrays (typically Ag or Au) of desired periodicity, by oblique angle metal deposition under high vacuum onto unidirectional nanorippled patterns fabricated by broad-beam ion sputtering of a solid dielectric surface (fig.1a). Using this method, periodic chains of elongated nanoparticles with dimensions and interparticle gaps below the resolution of lithographic techniques can be formed on large surface areas (> cm^2) in just a few tens of minutes (fig.1b). For light polarized along the particle chains, a high density of hot spots can thus be obtained leading to a stronger SERS signal compared to non-ordered nanoparticles. These very fine structured surfaces can then be coated with a very thin protective layer, which provides stability against ageing effects and temperature, but also enables repeated cycles of surface cleaning by usual solvents (fig.1c). Plasmonic nanostructures consisting of Ag nanoparticles embedded in an amorphous dielectric matrix (Al_2O_3 or Si_3N_4), developed at Pprime, have been already tested at the IMN lab on liquid samples with non-resonant bipyridine molecules and carbon nanotubes. As a proof of concept, they showed promising results (fig.2a): (i) detection of less than 10^{-6} mol/L, *i.e.* between 0.5 and 3 molecules per nm²; (ii) the surfaces have proven to be robust to alcohol cleaning as measurements were reproducible; (iii) aromatic gases present in environmental conditions workspaces were also easily detected. Also, by preventing direct interaction between the nanoparticles and the probed molecules, only electromagnetic effects contribute to the SERS intensity, which scales linearly with the concentration of analytes (fig.2b). Moreover, these substrates do not require special handling and can be stored at room temperature for months or even years. The capping layer protects the plasmonic nanostructures from damaging effects (e.g., oxidation or coalescence) caused by contact with solutions (*i.e.*, solutions of interest or cleaning solvents). These SERS substrates, which appear then non-selective to a specific molecular specie, open up promising opportunities for investigating mixtures of different components of interest with quantitative feedback in an intermediate detection range typically from 10^{-3} to 10^{-6} M.

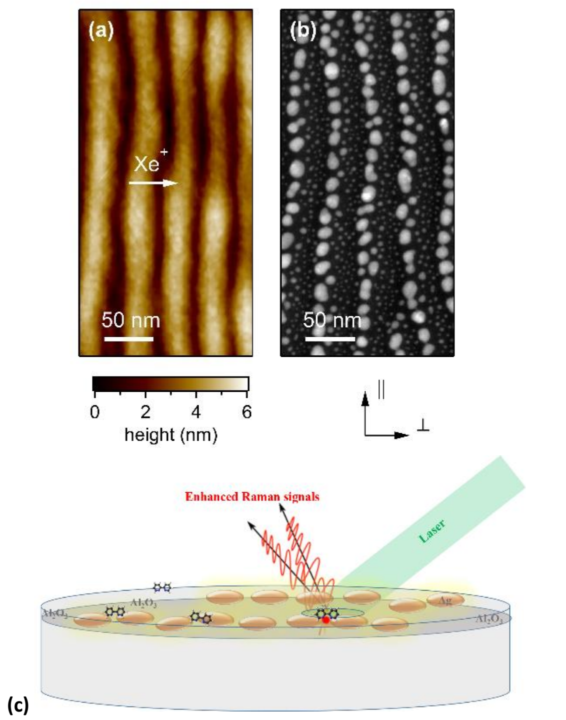

Fig.1 : (a) AFM image of an Al_2O_3 thin film etched with 1 keV-Xe^+ ions.
(b) HAADF-STEM plan view image of Al_2O_3-capped Ag nanoparticles grown on a rippled Al_2O_3 thin film.
(c) Sketch of the SERS substrate.

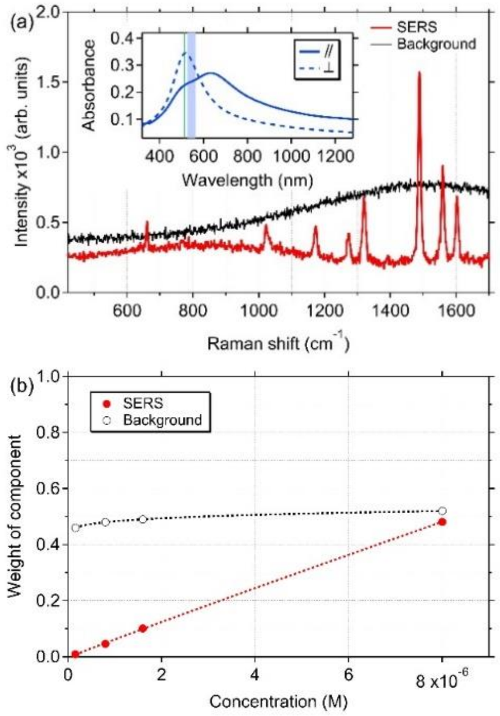

Fig.2 : a) Multivariate analysis of 108 SERS spectra recorded from an $Al_2O_3/Ag/Al_2O_3$ SERS substrate (5 nm thick capping-layer) at a laser excitation wavelength of 514.53 nm with transverse polarization of the excitation. Inset: Optical absorbance spectra of the trilayer with transverse or longitudinal polarization. (b) Respective weight of the 'background' and 'SERS' spectral components as a function of the bipyridine concentration.

Comparison and optimization of SERS substrates is often challenging because their rigorous characterization is complex and therefore frequently overlooked. Also, maximization of the electric field intensity at the surface of the protective capping layer, which causes enhanced Raman signals of the adsorbed molecules, results from a delicate balance between different parameters (including nature, size, shape, and organization of the metal nanoparticles, nature and thickness of the capping layer, excitation and Raman wavelengths) *vs* spectral position, amplitude, and width of the Surface Plasmon Resonance, polarization of the incident light, type of molecules, etc. From our previous studies and to go further into the investigation **several issues will be addressed during the PhD thesis:** Identification of alternative dielectric materials, Identification of alternative plasmonic species, Study of the far-field and near-field optical properties, Investigation of the SERS response of targeted species, Footsteps towards chemical sensors.

Thesis Schedule :

- The first year will be spent mainly in Poitiers to produce the first SERS substrates. Short stays at the IMN will be scheduled to perform initial tests and optimize the SERS responses.
- The second year will be spent in Nantes to develop and optimise the SERS measurement protocols with short stays at the Pprime institute to accompany the synthesis of optimised substrates.
- The last year will be dedicated to select the most efficient substrate to propose a basis for a viable sensor. Depending on the progress of the project, the PhD student will stay in Nantes or Poitiers to write his/her thesis manuscript.

Candidate profile

The PhD candidate must be graduated in Physics, in Material and Nano Science. He or she must show a strong motivation to carry out both experimental and numerical simulation works in collaboration with two research teams. An experience in electromagnetic modelling and in plasmonics would be greatly appreciated. The abilities to take initiatives and to work with autonomy are compulsory to properly carry out this thesis. The candidate must be open-minded and curious, able to learn by him(her)self through bibliographic studies.

Application: Send us as soon as possible

- your CV and a motivation letter,
- your Bachelor and Master transcripts,
- assessment letter from the Master2 internship supervisor
- possibly recommendation letters.

Selected candidates will be interviewed by visioconference.

Contacts :

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