High-Quality Hybrid Plasmonic Metasurfaces for Controlled Chemical Reactions at the Nanoparticle Scale.

Contact:

Nordin FELIDJ (nordin.felidj@u-paris.fr) ITODYS Laboratory, Université Paris Cité.

Project Summary:

Plasmonic metasurfaces composed of organized arrays of nanostructures (NSs) support collective surface resonances (RCS), resulting from long-distance interactions. Such modes generate optical quality factors that are rarely matched in the field of plasmonics. Recently, we have demonstrated hybridization from RCS modes. Similar to the hybridization of localized surface plasmon resonances (LSP) observed in short-range interactions, RCS hybridization leads to the emergence of bonding and antibonding modes, resulting from a symmetry-breaking in the array. Excitation of these modes accompanies unprecedented optical quality factors. In this thesis, we propose to develop gold and aluminum metasurfaces with various topographical configurations and employ them for induced chemical reduction reactions under RCS mode excitation.

General Scientific Context:

Metallic nanostructures (NSs) represent an exceptional tool for manipulating light at the submicron scale due to the excitation of localized surface plasmons (LSP).[1] These remarkable optical properties are characterized by a strong extinction in the far-field (dependent on the topographical parameters of NSs), accompanied by a strong electromagnetic field confined in the near-field of NSs. Such properties find applications in a wide range of fields, including photocatalysis, photo-thermal cancer therapies, and enhanced surface spectroscopies. However, due to their large radiative cross-sections and inherent non-radiative losses in metals, LSP exhibits relatively low quality factors Q (lower than $Q \lesssim 10-20$). The quality factor Q is defined as the wavelength of the resonance peak divided by the full-width at half-maximum. These values represent a limitation for most nano-optical applications. To improve the optical performance, a particularly versatile strategy is to generate long-range interactions between NSs, called collective surface resonances (RCS), which display quality factors beyond 100.[2] While a significant improvement in the quality factor has been demonstrated through array modes, much higher Q values can be achieved by hybridizing these modes, as recently demonstrated in simulations.[3,4] This hybridization has been shown to be related to a symmetry-breaking in the NSs array. Furthermore, due to the extended nature of these modes, a much richer hybridization scenario can be envisioned compared to the case of hybridizing LSP modes.

We have experimentally demonstrated the hybridization of RCS modes. Similar to the hybridization of localized surface plasmon resonances - LSP (observed in short-range interactions), RCS mode hybridization leads to the emergence of bonding and antibonding modes, resulting from a symmetry-breaking in the array. To our knowledge, very few experimental works have been proposed on this hybridization phenomenon, paving the way for engineering plasmonic systems with high-quality factors and wavelength adaptability. Such surfaces will be utilized to induce chemical reactions under plasmon excitation. Considering the expected high-quality factors, controlled and efficient reaction yields can be anticipated. To our knowledge, no chemical reaction experiment has been performed using RCS modes as initiators.

Objectives:

The objectives of the thesis project are twofold:

1. Investigate the optical properties of various hybrid metasurfaces composed of NSs (in gold or aluminum) exhibiting high-quality RCS modes with great wavelength adaptability. For this purpose, we will propose periodic arrays of NSs with varying sizes and multi-particle unit cells. Such systems offer strong array resonance, resulting from multiple coherent scatterings allowed by the periodicity of the array.
2. Explore chemical reduction reactions induced by the excitation of these RCS modes. We will propose two types of reactions: (i) the first consists of reducing a platinum salt into metallic platinum, selectively attaching it to the NSs (at the maxima of the electric field), thus paving the way for the development of bimetallic structures organized in an array; [5] (ii) the second envisaged chemical reaction involves the reduction of a DNO2 diazonium salt into a DNH2 diazonium salt. [6,7] This regio-selective reduction could enable the post-functionalization of negatively charged inorganic systems solely at the DNH2 level (e.g., negatively charged quantum dots - QDs).

Profile and Desired Skills:

The candidate should be an experimental physical chemist with a solid background in various spectroscopy techniques and expertise in the field of plasmonics. The candidate should also be familiar with the basics of the Finite-Difference Time-Domain (FDTD) method.

Bibliographic References

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