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Supervision

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PHD THESIS PROJECT

PLUTO - PLasmonic Ultra-fast Tunneling Optoelectronics

Summary / Abstract

Integrating plasmonics into nanodevices requires electrically driven nanosources. Tunnel junctions enable electrons to excite plasmons, creating fast, compact light sources. Despite these highly desirable features, their potential and scope is still underexploited in particular due to low efficiencies. The emission rate of plasmon sources is limited by low junction currents. Therefore we aim to study molecular-scale plasmonic tunneling junctions of the form of metal–molecule–metal junctions with tunable barriers enabling nonlinear emission effects such as non-classical emission statistics (bunching), intermittent emissions (flickering), overbias emissions, and unexplained spatial correlations between distant emission points. A molecular approach in this context is complementary to widely explored metal oxide barriers because by changing the molecular structure, we can control the tunneling barrier shape, control the tunneling mechanism, and dielectric properties of the junctions.

Principal 3i dimension: international. **Additional 3i dimension**: interdisciplinary

Keywords

- Information and Communication Technologies (optoelectronics, optical fibers...)
- Quantum technologies
- Nanophotonics (plasmonics, metamaterials, 2D materials, surfaces and interfaces, optomechanics)
- Materials (inorganic, semiconductor, organic, liquid crystal, photochromics)
- nanooptics
- scanning probe microscopy
- molecular junctions
- inelastic tunneling
- single photon sources

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PLUTO - PLasmonic Ultra-fast Tunneling Optoelectronics

Key Objectives

Our objectives: 1) understand the underlying mechanisms of the recently discovered nonlinear effects of plasmon excitation and 2) explore their temporal dynamics so as to control the dynamic and nonlinear properties of these plasmon sources through the chemical structure of the junction molecules. Using our novel scanning-probe nano-optics approach in conjunction with an approach involving large-area molecular tunneling junctions, we are in a position to bridge the gap between devices (in the Netherlands) and molecular-scale nano-optics (in France). Through molecular design, we can tune transport mechanisms and reach high tunneling rates where non-linear effects are important; this high current regime is difficult to reach with conventional metal oxide junctions. This approach should yield bright plasmon sources whose photon emission statistics we will study and single molecular devices which have potential as single photon sources.

Project

Context and state-of-the-art of Scientific Research project

Plasmonics has numerous applications in catalysis, sensors, nanolasers, super-resolution imaging, and ultralocal and ultrasensitive spectroscopies [1-5]. It exploits surface plasmons (SPs), electromagnetic waves coupled to electron density oscillations at the surface of metals such as gold, silver or aluminum. By exciting the SPs of metallic nanostructures, intense optical fields confined within nanometric volumes may be created, far exceeding the diffraction limit of light. Integrating plasmonics into an electronic nanodevice requires the development of electrically driven SP nanosources, which can convert electrical signals into SPs at the nanoscale [6-10]. One of the main strategies currently being pursued is the use of tunnel junctions formed from plasmonic electrodes separated by a nanometer-thick insulating layer or gap [11-17]. Electrons inelastically traversing the junction can excite the SPs of the electrodes. Based on this effect, extremely small and fast electrical plasmon sources may be realized. The mechanism involved, known since the 1970s [18], has been underexploited in devices until now due to its very low quantum efficiency (on the order of one quantum of optical excitation per million tunneling electrons). Recently, it has been shown that the external quantum efficiency of a device using this mechanism can be increased by several orders of magnitude by shaping the plasmonic electrodes to enhance the local density of electromagnetic states to which the tunneling current can couple [19]. However, the emission rate of these plasmon sources remains ultimately limited by the low current that can cross the junction per unit area, due to the lack of control over the thickness of the insulating layer (generally a metal oxide layer). In this context, the design of metal-molecule-metal tunnel junctions, where the molecules are present as monolayer, is a promising solution [14,20-22]. By varying the chemical structure of the molecules, the width and height of the potential barrier (and therefore the current flowing through the junction) can be controlled. Molecular engineering also allows one to manipulate the charge transport mechanisms across the molecules. In the high-current regimes achievable with molecular tunnel junctions, nonlinear emission effects have been observed, which are very promising for future applications but are still very poorly understood [23,24]. These effects include non-classical emission statistics (bunching), intermittent emissions (flickering), overbias emissions, and unexplained spatial correlations between distant emission points. Until now, these effects have only been studied using far-field techniques, which limits our understanding. In our project, localized excitation at the nanoscale and time-domain analysis of emission statistics will be used to investigate the mechanisms of these nonlinear effects and learn how to control them through the chemical structure of molecules.

Description

The use of plasmonic molecular tunneling junctions as electrical nanosources of light and surface plasmons (SPs) is a rapidly emerging field at the interface of nanophysics and chemistry. The temporal dynamics and recently discovered nonlinear effects in the emission from these inelastic tunneling-driven SP sources are still largely unexplored. The originality of our project lies in studying these effects at the nanoscale by replacing one of the two electrodes of these plasmonic tunnel junctions with the tip of a scanning tunneling microscope (STM) or atomic force microscope (AFM) in conductive mode. Thus, averaging effects will be greatly reduced and emission properties will be correlated with the local morphology and electrical conductivity of the molecular layer. The project has two objectives: to understand the underlying mechanisms using this novel scanning-probe nano-optics approach, and to learn how to control the dynamic and nonlinear properties of these plasmon sources through the chemical structure of the molecules forming the tunnel junction.

Impact.

The results of this project will have a considerable fundamental impact on understanding the microscopic phenomena involved in the emission of light and SPs in plasmonic molecular tunnel junctions and, more generally, on the link between the optical and charge-transport properties of molecular junctions. Our results will contribute to an understanding of the relationship between the chemical structure of molecules and the nonlinear effects, as well as the multiscale temporal dynamics, of these junctions observed under high current. In the long term, this understanding could lead to the design of new technologies, as molecular tunnel junctions are increasingly being considered for their neuromorphic properties, precisely linked to their nonlinear and non-stationary behavior. Moreover, our original experimental approach may inspire other studies on hybrid nanomaterials in optoelectronics.

Methodology.

The junctions will be based on alkanethiol and carbene chemistry, which yields stable plasmonic junctions that can be subjected to high voltages and currents [23-25]. The molecules will be synthesized in the lab of the 3i supervisor. They will be functionalized with redox groups (HATNA or quinone) associated with molecular switching, polarizable groups (halides) to control their charge transport properties, or electroluminescent groups (Ru-bpy) to harness the excitation of molecular exciton, see Fig. 1a-d. Self-assembled monolayers (SAMs) of these molecules will be prepared on atomically flat gold films on glass coverslips obtained by template stripping. Nano-optical scanning probe microscopy measurements will be performed in the lab in France, using an air-operating conductive AFM/STM head mounted on an inverted optical microscope. The STM or AFM tip will locally form a tunnel junction with the SAMs on gold. SPs excited by the tunneling current between the tip and the gold film will propagate along the gold film and their spatial distribution will be observed by optical microscopy of their radiative leakage in the glass substrate, see Fig. 1e-g [11,17]. The temporal dynamics of the emission will be analyzed by photon correlation. We will investigate the nonlinear effects and temporal dynamics of the emission as a function of current, at timescales from nanoseconds to seconds. The synthesis of new molecules, of varying lengths and chemical structures, will be guided by the results obtained from these measurements. Scanning probe nano-optical measurements performed on gold films coated with SAMs in France will be compared to larger-scale measurements performed using far-field optical microscopy on macroscopic junctions in the Netherlands. These latter junctions will be obtained by contacting the samples of SAMs on gold with a macroscopic EgaIn alloy top electrode [20]. Thus, the elementary mechanisms studied at the nanoscale will be linked to the macroscopic behavior of these plasmon sources.

Expected Results.

- Demonstration of higher SP emission rates and quantum efficiencies than state-of-the-art plasmonic junctions, by harnessing nonlinear effects at high currents.
- Comprehensive, multiscale description of the flickering emission statistics.
- Development a nanoscale switchable SP source out of few-molecule tunnel junctions and demonstration of single photon emission.

Timelines.

Year 1: Exploration of alkanethiol and carbene molecules with different lengths and different side groups to control steric hindrance. Preparation and characterization of the SAMs on gold films, junction properties with EGaIn alloy and AFM/STM techniques.

Year 2: In-depth study of flickering statistics from nanoscale junctions (AFM/STM) and large area junctions (EGaIn). Photon correlation, temperature dependent studies, impedance spectroscopy, photon emission efficiencies.

Year 3: Exploration of redox-active and electroluminescent molecules in the junctions.

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Facilities and quality of research environment available for the researcher

The environment of the CNRS and the University of Paris-Saclay offers an extremely rich framework for scientific interactions and collaborations. The Institute of Molecular Sciences of Orsay (ISMO) is a fundamental research unit in physics and physical chemistry, which has internationally recognized expertise in molecular physics and nanoscience. ISMO houses ≈ 40 lab rooms containing more than 50 experimental setups, most of which were developed in-house. The unit hosts ≈ 170 permanent staff, doctoral students, and postdoctoral researchers. ISMO houses 7 platforms and technical facilities in optical and electron microscopy, ultrafast laser spectroscopy, and surface science, as well as technical services in instrumentation, electronics and mechanics, and clusters for scientific computing. The researcher will use a unique experimental setup combining a conductive AFM/STM head operating in air with an inverted optical microscope equipped with high numerical aperture objectives, cooled cameras, an optical spectrometer, and single-photon counting modules connected to time-correlation electronics. Within the host team (Nanophysics@Surfaces), the researcher will interact with experts in optical microscopy and spectroscopy, STM/AFM, surface science, and electromagnetic modeling.

The proposed research bridges nanoelectronics, fabrication and surface chemistry, all of which are housed at the University of Twente. The Molecules Center and the Molecules & Materials Department are already active in surface modification, molecular switches, polymer chemistry, and characterization, hence the infrastructure to synthesize and characterize new molecular materials is well established. The University of Twente houses state-of-the-art clean room facilities required to fabricate the proposed plasmonic molecular tunnelling junctions. Within MESA+ and the Device Research Area, the know-how to design and conduct high precision opto-electronic measurements are available. The group of the 3i co-supervisor (Hybrid Materials for Opto-Electronics) houses 4 EGaIn setups to fabricate molecular plasmonic tunneling junctions, cryogen free probe station, parameter analyzers, impedance analyzers, placing the group in an ideal position to investigate charge transport mechanisms in detail. This group also has a line of research on optics and molecular electronics with home-build setups for in situ spectroscopy and imaging while measuring the electronical properties.

3i Dimensions - international; interdisciplinary

Description and expected outcomes

The proposed project fulfills both the international (primary) and interdisciplinary dimensions, as it involves a collaboration between a chemistry laboratory in the Netherlands and a physics laboratory in France. The PhD supervisor at the Institute of Molecular Sciences in Orsay is a physicist, while the 3i co-supervisor in the Department of Molecules & Materials at the University of Twente is a chemist. The recruited PhD student will spend 12 months of their PhD in the 3i co-supervisor's group, training in the synthesis of organic molecules and their deposition on surfaces. During the 24 months spent in France, the student will use scanning probe microscopy and optical microscopy to perform the measurements described in the project (see Gantt chart in Fig. 2). The benefits of this international and interdisciplinary collaboration are numerous (see diagram in Fig. 3). These outcomes include the training of interdisciplinary students, the founding and strengthening of a collaboration between our two laboratories, the expansion of our areas of expertise through skills transfer, potential applications for European calls for project and network funding, and the organization of binational workshops. Furthermore, the project's scientific results will be published in open access journals with peer review and presented at international conferences.

Approximate timeline of internships / external stays corresponding to the 3i dimension

- **Year 1 (October 2026 – September 2027)**

Semester 1 at the University of Twente. Training in molecule synthesis, preparation and characterization of SAMs and junctions. Preparation of a batch of SAMs on gold film for experiments at ISMO.Semester 2 at ISMO. Training in the use of optical microscopy, STM, and AFM. Characterization of the electrical and optical properties at the nanoscale of the SAMs on gold prepared at the University of Twente.

- **Year 2 (October 2027 – September 2028)**

Semester 1 at the University of Twente. In-depth study of the flickering statistics of large-area junctions. Temperature-dependent measurements, impedance spectroscopy, measurement of quantum efficiencies. Synthesis of redox-active and electroluminescent molecules. Preparation of a second batch of SAMs on gold film for ISMO.

Semester 2 at ISMO. In-depth study of emission time-domain statistics and photon correlation measurements on nanoscopic junctions formed by the tip of AFM or STM. Transfer to ISMO of the gold film and SAM preparation techniques.

- **Year 3 (October 2028 – September 2029)**

Semester 1 at ISMO. Nano-optics study using STM/AFM on SAMs of redox-active and electroluminescent molecules prepared at ISMO using the method learned at the University of Twente and transferred to ISMO.

Semester 2 at ISMO. Dissemination of results obtained (writing articles), writing the thesis, and preparing for the thesis defense.

ISMO will provide financial support to partially cover additional related expenses.

Profile of PhD fellow

PhD studies and research work require curiosity, creativity, rigour, teamwork, and organisational skills. A minimum B2 level of English is mandatory. The below criteria are specific to the thesis project.

mandatory	Academic background in physics, physical chemistry, or chemistry..
very desired	Work/internship experience in experimental physics and / or in experimental chemistry.
advantageous	Theoretical and / or experimental knowledge in optics, nanophotonics, and plasmonics.
advantageous	Theoretical and / or experimental knowledge in chemical synthesis
advantageous	Work/internship experience in cleanroom based micro/nanofabrication, electrical characterization, optical microscopy, quantum optics (photon statistics), and / or scanning probe microscopy.

Ethics issues in the project as per Horizon Europe Ethics Self-assessment

Section 1. Human embryonic stem cells (hESCs) and human embryos (hEs)			No
Section 2. Humans	No	Section 3. Human cells and tissues	No
Section 4. Personal data	No	Section 5. Animals	No
Section 6. Third Countries	No	**Section 7. Environment, health and safety**	**Yes**
Section 8. Artificial Intelligence	No	Section 9. Other ethics issues	No
Section 10. Crosscutting issue: potential misuse of results			No

7. Environment, health and safety

All French labs are required to have health and safety procedures in place, which takes into account the use of high-energy light sources such as lasers of class 3 and above, and the use of hazardous / toxic chemical and biological products. The institution and the laboratory comply with the highest safety requirements and PhD fellows have mandatory health and safety training, with additional training if required.