PEOPLE MARIE CURIE ACTIONS
Marie Curie Career Integration Grants (CIG)
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"**ENSOM**" Project
Electrochemical **N**ear-fied **S**canning **O**ptical **M**icroscopy:
Manipulation and characterization at the nanoscale.

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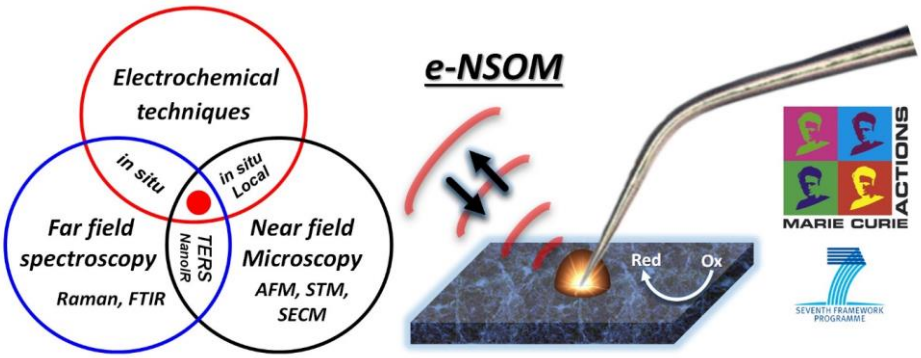


FINAL PUBLISHABLE SUMMARY REPORT

The ENSOM project aimed at developing and delivering a cutting edge analytical tool to provide unprecedented diagnostic capabilities for the characterization of nano/micromaterials of interest for energy conversion and storage, for nano-electronic and catalysis, among others. The instrument we have developed, an electrochemical near-field scanning optical microscope (e-NSOM) will be used as a "Nano/Microlab station" that will enable surface locale modification or characterization using a nanoelectrode and immediate composition mapping with a nanometer spatial resolution (nanospectroscopy Raman). This combination of several individual functions in a single unit will not only bring new insights in the fundamental understanding of micro and nanomaterials but also open new routes to the functionalization or modification of material at the nanoscale.

Project objectives

1- **Instrumentation development**
- *Nano hybrid probes used as topography / nanosource of light and nanoelectrode*
- *Local electrochemistry and spectroscopy measurements (Raman).*
- *Electrochemical **TERS**: Tip Enhanced Raman Spectroscope (e-NSOM)*

2- **Preliminary diagnoses at the nanoscale**
- *Alteration and analysis of molecules on surfaces (grafting, etching, redox processes)*
- *Evaluation of transport properties in micro/nanomaterials*

I- Work carried out between 2014 & 2017:

✓ ***Nano hybrid probe development -*** TERS active probes have been manufactured by electrochemical etching of gold and silver wire. The obtained tapered tips were partially insulated to be also used as micro/nanoelectrodes.

✓ ***Building of the e-NSOM platform at LISE -*** a high resolution microRaman spectroscope equipped with 5 laser lines has been optically coupled to two Scanning probe microscopes (SPM with AFM/STM/shear-force measurement modes). The use of a robust optical coupling and of a high numerical microscope objective mounted on piezo stage allows a precise and stable positioning of the excitation laser sources at the apex of the gold or silver tips, prerequisite for strong and stable TERS signal at the tip-sample junction. The setup enables TERS measurements on transparent samples in a transmission configuration and on non-transparent samples in a reflection configuration.

✓ ***Instrumental development for electrochemical TERS -*** We have developed a 4 electrode electrochemical cell and have integrated a bipotentiostat to the TERS equipment (hardware and software) to polarize either the substrate, the tip or both. A long distance immersion objective has been also introduced in the TERS reflection configuration to maximize the TERS signal collection in liquid. Similar developments are still under way to implement EC-TERS also in the transmission mode.

✓ ***Diagnoses at the nanoscale -*** Molecular self-assembled monolayers on gold (SAM) with no µRaman signature were scrutinized by TERS in liquid. The electrochemical transformation of such SAM was studied by EC-TERS.

II- A description of the main results achieved:

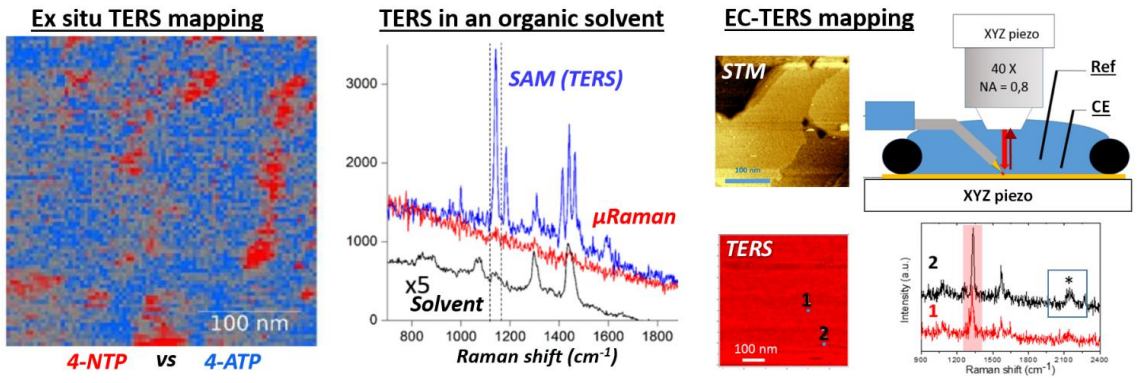
✓ ***Manufacturing of nanoprobes for TERS imaging –*** Gold nanotips (and silver recently) with sub-15nm radius of curvature suitable to achieve molecular (rotaxane molecules) and atomic resolution (HOPG) and tunable tapper angle were engineered using electrochemical techniques. Strong TERS signal obtained with gold and silver tips on model samples (CNT and self-assembled monolayers: azobenzenes, 4-NTP on gold surfaces), even in liquid.

✓ ***First worldwide TERS in an organic solvent -*** The efficiency of our TERS setup has been demonstrated by extracting the TERS signal of a self-assembled monolayer (SAM) covered with an organic solvent which the Raman response overlaps with the one of the SAM.

✓ ***First worldwide TERS imaging in liquid -*** To maintain the optical coupling (TERS tip laser) while imaging a sample in liquid is not trivial. A 300 x 300 nm² (900 pixel) hyperspectral TERS image of a SAM covered with a thin layer of organic solvent has been obtained in 2016 in 90s (0.1s per pixel/spectra).

✓ ***EC-TER spectroscopy -*** An original configuration where a TERS active tapered electrode had been partially insulated (microelectrode), directly functionalized with a redox active SAM (4-NTP) and positioned in the electrolyte at the focal point of an immersion objective has been developed. Strong potential dependent TERS signatures have been extracted providing important insights in the understanding of the 4-NTP reduction process. This configuration can be applied to the study of complicated molecular architectures with redox properties.

✓ ***EC-TERS imaging -*** STM/TERS imaging of a SAM has been successfully achieved using a 4 electrode configuration (Substrate, insulated gold tapered tip, counter & and reference electrode) and an immersion objective.



From left to right, ex situ STM-TERS mapping of 4-NTP/4ATP SAM mixture (300 x 300 nm²), TERS signature of a SAM covered by a layer of organic solvent, TERS imaging in water of a 4-NTP SAM on gold imaged using the EC-TERS cell, a partially insulated gold STM-TERS tip and an immersion objective. Similar developments for EC-AFM-TERS are under way.

III- Potential impact and use

- Envisioned breakthroughs in the understanding of functional nanomaterials, modified, observed and characterized under the condition of their operation, with immediate industrial application (catalysis, sensors, nanoelectronics).

- Development of advanced near-field techniques (electrochemical TERS), with the aim of facilitating and popularizing their use for the characterization materials at the nanoscale.