Electrocatalysis scrutinized by tip-enhanced Raman spectroscopy

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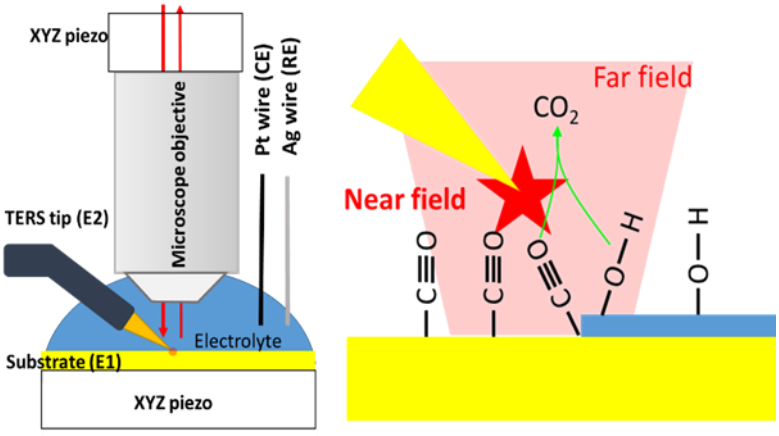
With the increase in complexity of materials to improve or even create new functionalities, there is a concomitant need for powerful analytical techniques adapted to unravel the underlying mechanisms when they operate. Ideally, they should be implemented under operando conditions, as close as possible to their future potential application. This is particularly important at the nanometric scale since the material structure evolution during operation is the key of its efficiency.

For example, in electrocatalysis, reactions are triggered by the electrode potential, with the aim of minimizing overpotential and increasing the catalyst turnover. Nowadays, there is often a need for complementary (*i.e.* spectroscopic) measurements for example to take into account spatial inhomogeneities or check the effective presence of a reactive intermediate since electrochemistry only "sees" the average current produced does not provide access to local heterogeneities or temporal fluctuations.

Recently, we developed approaches derived from Tip Enhanced Raman Spectroscopy (TERS). This technique couples STM or AFM with Raman spectroscopy to provide a local spectroscopic signature and therefore allows identification of chemical species at the nanometric scale. We are among the few groups able to implement TERS in electrochemical conditions.[1] Our methodology is now sufficiently robust to be transferred to systems relevant to electrocatalysis, which will be the topic of our new project funded by the French national research agency (ANR). Herein, we will apply electrochemical TERS to follow electrocatalytic conversion of formic acid and CO onto Pt and Pd/Pt surfaces. We will first implement TERS onto Pt surfaces with a reference system. Comparison with gold that is more often used will provide key information about the enhancement in those specific conditions. Then, the same system will be scrutinized under electrochemical conditions, *i.e* using a 4 electrode configuration within an electrolyte. The aim will be to obtain images at different substrate potentials. We will in the project work with well-oriented Pt surfaces modified with (sub) monolayers of Pd, to probe the vibrational properties of a range of small molecules interesting in the field of energy. The project is of fundamental nature, and we are seeking a candidate with an expertise in electrochemistry and possibly spectroscopy and/or scanning probe microscopy, with a strong taste for handling state of the art equipment.



Principle of electrochemical TERS and schematic of measurements that will be performed.

[1] Capturing electrochemical transformations by tip-enhanced Raman Spectroscopy. T. Touzalin, S. Joiret, E. Maisonhaute, I. T. Lucas, *Current Opinion in Electrochemistry*, 2017, 6, 46-52. Electrochemical tip-enhanced Raman spectroscopy imaging with 8 nm lateral resolution. T. Touzalin, S. Joiret, I. T. Lucas, E. Maisonhaute, *Electrochemistry Communications*, 2019, 10.1016/j.elecom.2019.106557.