Sorbonne Université/ China Scholarship Council program 2020

Thesis proposal

Title of the research project: Time-resolved electrochemical Raman spectroscopy – towards understanding electrocatalysis

Keywords: Surface Enhanced Raman Spectroscopy, Electrochemistry, Electrocatalysis

Joint supervision: no

Joint PhD (cotutelle): no

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Institution: Sorbonne Université………………………………….

Doctoral school (N°+name): ED ED 388 Chimie Physique et Chimie Analytique de Paris Centre

Research laboratory: Laboratoire Interfaces et Systèmes Electrochimiques……………………..

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Time-resolved electrochemical Raman spectroscopy - towards understanding electrocatalysis

Abstract: This project will aim at gaining information onto electrocatalytic systems in operando conditions. For that, electrochemistry will be coupled to Raman spectroscopy. We will benefit from the new methodology called EC Tip-SERS to identify chemical intermediates and possible phase transitions of the active material. The temporal resolution of the experiment will be optimized to catch short life-time species.

1) Study context

Electrochemistry, and more specifically electrocatalysis, have a key role to play in the global energetic transition to minimize fossil energy consumption. However, the development of new electrocatalysts necessitates fundamental understanding of the underlying mechanisms. What are the chemical structures of reaction intermediates? What are the oxidation states and phases involved at different potentials?
In this context Raman spectroscopy has revealed to be an efficient tool, since it provides a chemical identification and can be readily implemented in liquid. However, the Raman signal usually needs to be enhanced. Typically, gold or silver nanoparticles are used for that purpose. Nevertheless, the LISE researchers recently developed an alternative called ElectroChemical Tip-SERS (EC Tip-SERS). The present project aims at adapting this methods to electrocatalytic systems.

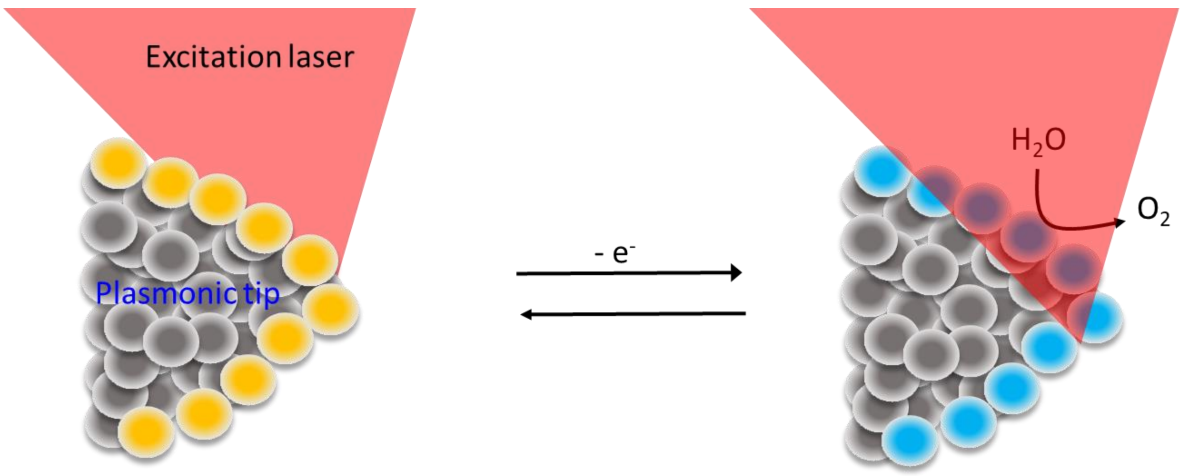
2) Details of the proposal

The EC Tip-SERS approach relies on the use of a tapered gold or silver wire. The tip apex provides a specific Localized Surface Plasmon Resonance (LSPR) that can be excited with a 633 nm laser. As a consequence, the local electric field is much larger which allows to recover a Raman signal from a small amount of material present on the tip. Besides, the tip may be used as a microelectrode so that electron transfers can be triggered in a similar way to what is performed in conventional electrochemistry. Presently, only the proof of concept has been established onto self-assembled monolayers. The project will explore two different aspects:

- *Electrocatalytic materials.* In a first step a layer of catalyst (*e.g.* cobalt, nickel or a molecular system) will be deposited on the tip. The electrodeposition conditions will be optimized so as to provide a maximum signal upon electrochemical polarization in a different solution. We aim at working onto oxygen reduction or water oxidation in a first step, but other reactions may also be considered.

- *Temporal resolution.* Since the tip size can be reduced to micrometric dimensions, the timescale of the electrochemical measurements can be reduced to a few microseconds. This however necessitates a proper synchronization of electrochemical and Raman measurements. This opens the route towards characterization of short life-time intermediates.

Once the proof of concept will be established for model systems, the technique will be applied to those presenting the largest activity.



Sketch of the EC Tip-SERS experiment. A gold or silver tip is covered with an electrocatalytic material. The tip potential can be varied to trigger an electrocatalytic reaction while the Raman spectra provide information about the reactive intermediates.

3) References

T. Touzalin, S. Joiret, E. Maisonhaute, I.T. Lucas, Complex Electron Transfer Pathway at a Microelectrode Captured by in Situ Nanospectroscopy, Anal. Chem., 89 (2017) 8974-8980.

4°) Profile of the Applicant (skills/diploma…)

The applicant should have strong background in physical chemistry, and more specifically in electrochemistry and possibly spectroscopy. An important part of the project concerns instrumental development, which requires maturity and a taste for interfacing different experiments (here electrochemistry and Raman spectroscopy).

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