AAP China Scholarship Council – CSC 2023

PROJET DE RECHERCHE DOCTORALE (PRD)

Titre du PRD : Operando investigation of electrocatalytic reactions thanks to electrochemical tip enhanced Raman spectroscopy

DIRECTION de THESE

Porteuse ou porteur du projet (doit être titulaire de l'HDR) :

NOM : MAISONHAUTE

Prénom : Emmanuel

Titre : PU ou Autre :

Section CNU : 31

Email : emmanuel.maisonhaute@sorbonne-universite.fr

Unité de recherche : Code (ex. UMR xxx) et Intitulé : UMR8235

Ecole doctorale de rattachement : ED388 – Chimie Physique et Chimie Analytique de PC

Nombre de doctorants actuellement encadrés : 0

CO-DIRECTION de THESE (HDR) ou CO-ENCADREMENT (Non HDR) :

Porteuse ou porteur du projet (doit être titulaire de l'HDR) :

NOM :

Prénom :

Titre : PU ou Autre :

Section CNU :

Email :

Unité de recherche : Code (ex. UMR xxx) et Intitulé :

Ecole doctorale de rattachement :

Nombre de doctorants actuellement encadrés : 0

CO-TUTELLE INTERNATIONALE envisagée : OUI × NON

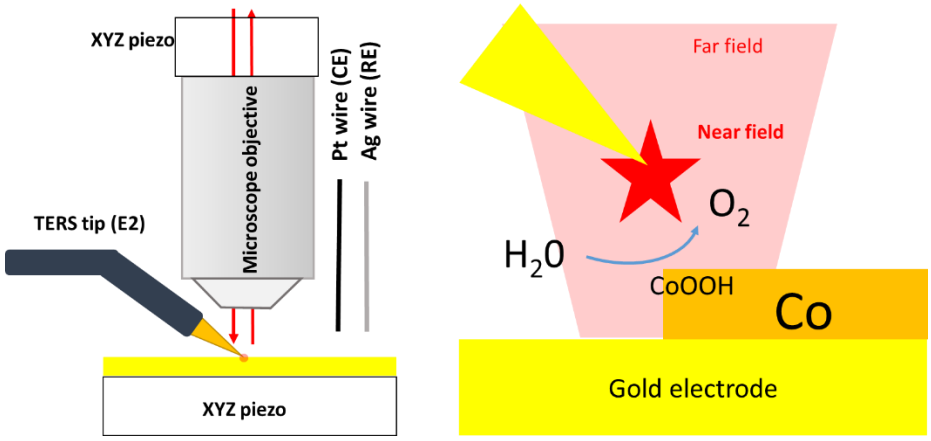
DESCRIPTIF du PRD

Electrocatalysis scrutinized by tip-enhanced Raman spectroscopy

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 *in situ* 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 increase 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. Nevertheless, implementing TERS in electrochemical conditions is difficult because the Raman laser should be focused onto the STM or AFM tip through the liquid layer.[1] Our methodology is now sufficiently robust to to be applied onto systems relevant to electrocatalysis. After a training period on electrochemical TERS, two systems of interest. The first one will concern 2D materials such as MoS_2 that has been spotted as a good catalyst for H^+ reduction. In a second approach an active material such as cobalt oxide, as reference system for water splitting, will be electrodeposited.[2] In both cases the aim will be first to register spectra at fixed positions on the electrode but at different potentials. Next, imaging will be performed with the aim of identifying active areas on the surface.



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

References:
[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.
[2] *Mechanism of Oxygen Evolution Catalyzed by Cobalt Oxyhydroxide: Cobalt Superoxide Species as a Key Intermediate and Dioxygen Release as a Rate-Determining Step*. A. Moysiadou, S. Lee, C.-S. Hsu, H. M. Chen, X. Hu, Journal of the American Chemical Society, **2020**, 142, 11901-11914.

AVIS de l'Ecole Doctorale :