

PhD at Université de Rennes 1 - France  
Institut des Sciences Chimiques de Rennes

Starting: October the 1<sup>st</sup>, 2018

Duration: 3 years

Keywords: surface functionalization, diazonium, nanoparticles, electrocatalysis



### Topic: Biomimetic and functional interfaces / nano-objects for electrocatalysis

The modification of surfaces with functional molecules allows a fine control over the interfacial properties of materials, while preserving their intrinsic properties. This lead to the development of innovative materials dedicated to analytics (higher sensibility / selectivity for diagnosis and therapeutics in (nano-) medicine for example) or to catalytic purposes (better performances and selectivity of processes). Control of the phenomena taking place at the solid (material) / liquid (analyte, electrolyte) interface is crucial for developing effective technologies.

We have demonstrated in the laboratory that the chemical grafting of organic molecules, using aryldiazonium chemistry, allows the introduction of molecular functions and/or nano-structuring on metallic surfaces in a very effective, versatile and extremely robust way, whether on massive or divided materials (spherical nanoparticles, nanorods, nanowires). It is then possible to control the interface of the metallic materials at the molecular scale, thanks to the grafting of a single organic monolayer.

During this Ph.D., a new concept based on the control of the interfacial reactivity through the molecular functionalization of catalytic surfaces will be explored, on both massive and divided materials. This new concept is bioinspired, notably by metalloenzymes capable of catalyzing complex processes, where multiple electronic exchanges are coupled with protons transfers, with high efficiency and selectivity. These multi-electronic processes allow the activation of small fuel molecules ( $O_2$ ,  $H_2$ ,  $H^+$ ,  $CO_2$ ,  $H_2O$ ), which still remains a challenge for both fundamental studies and applications in various fields (energy, environment, eco-processes). In particular, activation of small fuel molecules will give access to a clean and sustainable source of energy, with the possibility to convert chemical energy into electrical one with a maximal efficiency.

Through the grafting of functional macrocycles or through the molecular nanostructuring, biomimetic interfaces and nano-objects will be developed in order to reach a better selectivity / efficiency regarding these multi-electronic processes. The implemented methodology for designing these objects will be based on the recognized expertise of the host laboratory in the field of surface functionalization (*Nature Commun.* 2012, DOI 10.1038 / ncomms2121, *J. Phys. Chem. C* dx.doi.org. / 10.1021 / jp5052003; *Chem. Commun.* DOI 10.1039 / c6cc04534k, *Current Opinion in Electrochemistry* doi.org / 10.1016 / j.coelec.2017.11.003). The functionalized surfaces and nano-objects will be designed, realized and characterized in the host laboratory, employing various techniques (spectroscopy, electrochemistry, electronic microscopies). The strategy will then be evaluated by considering fundamental electrocatalytic reactions, namely conversion of  $O_2$ , reduction of  $H^+$  or  $CO_2$ . The catalytic reactivity and the interfacial phenomena will be thoroughly studied by electrochemical techniques and by electrochemical microscopy (SECM). Complementary techniques (Raman, in particular) will be also used for the identification of transient species. Syntheses and molecular modelling will be implemented, if needed.

**Required skills:** The candidate should be trained in at least one of the following fields: electrochemistry, physical chemistry of surfaces, biochemistry/biotechnology and/or synthesis of nano-objects.

**Funding** for 3 years from the Research Ministry (1374 € netto per month).

**Supervisors:** Corinne Lagrost and Yann Leroux (CR CNRS)

Should you be interested, please send a CV and a motivation letter before June, 15<sup>th</sup>, 2018.

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