

Title	Unraveling the Electroreduction Mechanism of Nitrate to Ammonia: In-situ Electrochemical Scanning Tunneling Microscopy Analysis at Metal-Centered Porphyrins
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# months (min.3)	6 months

Project description (2 pages max):

The electrochemical nitrate reduction reaction (NO₃RR) is a potentially attractive approach to nitrogen cycle remediation as it can be powered by sustainable energy sources to form more environmentally benign and/or value-added nitrogen-based chemical products. Moreover, when ammonia is the product of NO₃RR, it offers an alternative route to this important industrial material and carbon-free fuel compared to the traditional thermal Haber-Bosch process. However, because the reduction of NO₃⁻ to NH₃ involves the coupled transfer of multiple electron and proton equivalents, NO₃RR selectivity is a significant challenge as various products are accessible (e.g., NO₂⁻, NO, N₂O, N₂, NH₂OH). Furthermore, what makes a catalyst truly effective remains largely unknown, and the development of novel electrocatalysts is complex due to a lack of fundamental information on how the active sites should be designed for properly working. Therefore, a clear understanding of the electrocatalysis involved in NO₃RR is crucial. Among different approaches Electrochemical Scanning Tunneling Microscopy (EC-STM) it has demonstrated to be a useful technique for operando/in-situ evaluation of electrocatalytic processes. EC-STM coupled with more conventional voltammetric measurements can indeed rationalize the catalytic behavior of electrocatalytic materials.

Metal phthalocyanines and porphyrins are known to act as catalysts for several small molecule reduction including O₂ and CO₂ and are indeed good model systems for mimicking metal nitrogen sites (M-N_x) present in carbon materials, which represents a class of material with high promises in term of activity and scalability. Co and Fe protoporphyrins, directly adsorbed on pyrolytic graphite have been also utilized for catalyzing the electrochemical reduction of nitrate, showing different selectivity and activity depending on the metal center.¹ Therefore, it becomes obvious that we can use metal macrocycles as model systems to describe how the catalytic activity of M-N_x centres can be affected by metal type. If the support is a single crystal conductor (Au(111), HOPG, etc.), a highly ordered surface suitable for self-assembly characterization is obtained and the molecular system can be characterized in a typical three electrodes electrochemical cell for standard electrochemical measurements or even probed by means of EC-STM. In this context, the aim of this project is to employ EC-STM techniques to carefully probe metal-octaethylporphyrin functionalized surfaces (M = Fe, Cu, Ni, Co, Mn, Cr, Pt, etc.) towards the NO₃RR. It is worth mentioning also the good stability of the adsorbed layer, since an almost perfect layer was observed also after a long series of cyclic voltammetries, up to relative extreme reductive potential for gold electrodes (-0.5 V vs RHE).

The project will take advantage of the consolidated experience of EAEG groups in the field of oxygen reduction reaction,^{2,3} and hydrogen evolution reaction electrocatalysis,⁴⁻⁶ employing the STM based techniques.

EC-STM will serve as a characterization technique for visualizing the active site and the evolution of the active site during the electrocatalytic process (Figure 1). If the metal center is indeed the active site, the electrocatalytic process is expected to occur via an inner-sphere electron transfer mechanism. For example, the coordination of NO_3^- at the metal porphyrin centre can be envisaged as variations in tunneling current when probed by the STM tip. NO_3^- can be initially coordinated by the catalytic site before being reduced into reaction products, which in turn are supposed to be visualized according to a different tunneling current response. For instance, O_2 adsorption was characterized on a metal porphyrin functionalized Au(111) surface, evidencing a clear change in the STM contrast and its associated topographic bump when O_2 was adsorbed on the Fe centres. This gains extreme relevance because it really allows to employ EC-STM as a mean of characterization for reaction mechanisms, especially for their first step which is often ascribable to adsorption on the catalytic centres.² This approach enables precise identification of the active site and sheds light on fundamental aspects of the catalytic mechanism by the intermediate's identification upon the screening of the possible reaction intermediates or products (e.g., NO_2^- , NO , N_2O , N_2 , NH_2OH). On this regard, the effect of metal center, the applied potential, the effect of the pH and of the electrolyte or of the electrodic support will be evaluated for understanding how these experimental conditions affect the activity and selectivity of the active site for the NO_3RR .

Moreover, the facilities of EAEG group feature a RRDE with replaceable single crystal disk insert, which allows to access to additional mechanism information utilizing an identically functionalized substrate employed for EC-STM characterization. An EC-Raman is also available to further explore these molecular arrays, and a GC-MS/TCD will be useful for the quantification of NO_3^- reduction products. As the EC-STM is utilized to investigate modeled systems, computational methods are implemented in collaboration with the Theoretical Chemistry Group of the department, to enhance the interpretation of the experimental data. A computational approach to the study of structure, thermodynamics and kinetics of the polymorphic systems adsorbed on Au(111) surfaces will be carried out to characterize the nitrate ion reduction mechanism at the atomistic level. Quantum mechanical approaches based on density functional theory (DFT) will be adopted to access the structure and the relative stability in terms of Gibbs free energy, of the reaction intermediates. The hexagonal porphyrins adsorption pattern on Au(111) surface is nowadays well described and accepted, but DFT calculations can still provide relevant information regarding the strength and the orientation of the bond that nitrogen oxides form with the metal centre, and are already widely integrated alongside STM experiments. For instance, oxygen can bond with the metal centre both with the *end-on* and *side-on* form, while nitric oxide is known to bond with the nitrogen side of the molecule. The required estimation of the enthalpy of hydration and of the zero-point energy will be carried out at the same level of theory. As the solution is rich in ions, and a large density of charges is expected on the surface, the effective local electric potential will be required to correct the calculation of the relative stability of the intermediates. To this purpose, classical molecular dynamics simulations on extended portions of the surface and the surrounding liquid environment will be carried out to estimate the electrostatic potential as function of the distance from the surface.

In addition, the capability to spend a period of time at the Department of Chemistry of the Technical University of Munich in the group of Prof. Dr. Ueli Heiz, under the supervision of Dr. Friedrich Esch will allow to access a decisively new type of Fast-EC-STM, which does not find equal among groups working in this field.⁷⁻¹⁰ The instrument is indeed capable of recording STM images with video frequency up to 100 frames per second, thus being really able to probe the dynamics of a certain catalytic process. Another brilliant feature of the Fast-EC-STM is the so-called "atom tracking". This means that a dithering movement is applied to the STM tip and a gradient error signal is extracted for the x- and y- directions as lateral feedback. The result is that the tip can be kept fixed on a specific position with atomic resolution within a time frame of milliseconds. Thanks to this special feature, the Fast-EC-STM is expected to monitor the behavior of one individual metal centered porphyrin, giving access to precious information on the dynamics of the electrochemical process in which it is involved (redox state changes, evolution of electrocatalysis of small molecules). Thanks to an innovative statistical method based on Python code, the captured images are easily analysed, assessing height variations of the adsorbed porphyrins when the applied voltage is altered.

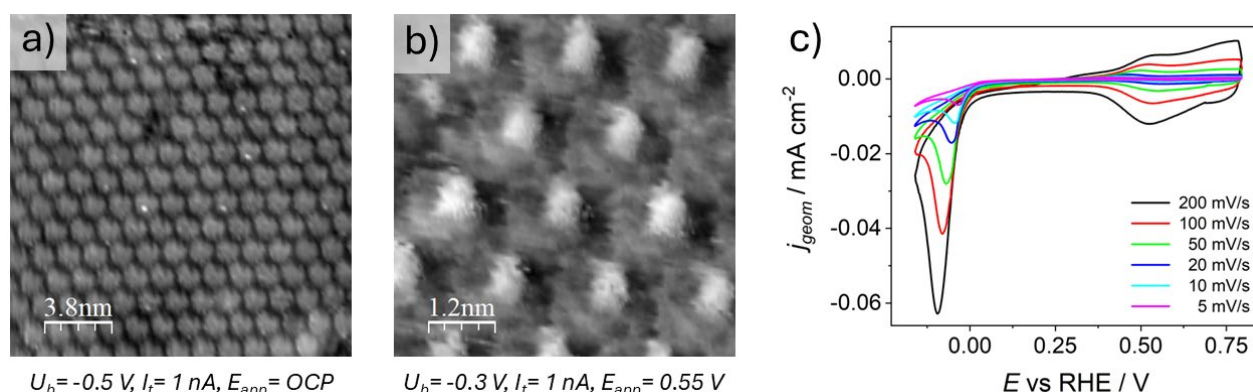


Figure 1. High-resolution EC-STM images of FeOEP@Au(111) system in Ar-purged **a)** HClO₄ 0.1 M and **b)** HClO₄ 0.1 M + HNO₃ 1 μM. **c)** Cyclic voltammetry of FeOEP@Au(111) system HClO₄ 0.1 M + KNO₂ 1 mM.

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