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):

Nitrate (NO_3^-) is considered one of the top 10 drinking water pollutants above the maximum contamination level (MCL > 10 mg NO_3^- L^{-1}), because this contaminant poses alarming risks to human health, it can trigger cancer, thyroid problems, and adverse respiratory effects.[1] Nitrate contamination accounts for 4% loss of fresh water from sources such as aquifers in most developed regions of the world, such as in the USA and Europe.[2] Such increasing and continuous losses of groundwater from NO_3^- contamination have led to the development and application of various physical, chemical, and biological NO_3^- remediation methods in the attempt to mitigate contamination along to severe regulation and limitation for nitrate usage and spilling.[3]

In this context, 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 NO_3^- to NH_3 involves the coupled transfer of multiple electron and proton equivalents, NO3RR selectivity is a significant challenge as various products are accessible (e.g., NO_2^-, NO, N_2O, N_2, NH_2OH). 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. On this regard, there currently is a continuously growing interest towards *operando* characterization techniques. Their main advantage consists in the ability of probing the catalyst at the same time it is operating, leading to more accurate and realistic results in terms of number and type of involved active sites, as well as the possibility to detect reaction intermediates.[4] Among different approaches Electrochemical Scanning Tunnelling 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 electrodic materials.

Metal phthalocyanines and porphyrins are known to act as catalysts for several small molecule reduction including O_2 and CO_2 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 pyro-

lytic graphite have been also utilized for catalyzing the electrochemical reduction of nitrate, showing different selectivity and activity depending on the metal center.[5] 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. The project will take advantage of the consolidated experience of EAEG and INCAT groups in the field of oxygen reduction reaction,[6,7] and hydrogen evolution reaction electrocatalysis,[8–10] 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. 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 envisage 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.[6] 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 intermediated 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 NO3RR.

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. The collaboration with the INCAT group can open to the very same system but in UHV conditions. Deposition of metallated porphyrins onto Au(111)/HOPG support in ultrahigh vacuum (UHV) environments is a common practice in surface science studies aimed at probing porphyrins' properties and surface interactions at atomic and molecular scales. Techniques such as X-ray photoelectron spectroscopy (XPS), UHV-STM, and low-energy electron diffraction (LEED) are employed for layer analysis. Metallated porphyrins are sublimated onto prepared substrates from a heated pyrolytic boron nitride crucible within the UHV chamber, with deposition rate and temperature carefully controlled to achieve the desired layer coverage and uniformity. After deposition, samples are transferred to analysis chambers without exposure to ambient conditions for XPS, STM, and LEED. XPS reveals element binding energies and molecular-substrate chemical interactions, while STM images elucidate molecular organization, including islands, edges, and defects. LEED can confirm the STM images but within millimetric-scale, diffraction patterns can display well-defined porphyrin layer superstructures. By integrating these techniques, comprehensive insights into the chemical composition, electronic structure, and spatial arrangement of deposited layers under ideal UHV conditions are achieved. 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. Friedric Esch will allow to access a decisively new type of Fast-EC-STM, which does not find equal among groups working in this field.[11–14] 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).

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