

Investigating the stability of covalent metal-porphyrin network under oxygen evolution/reduction reaction

A. K. Vestergaard¹, J. V. Lauritsen¹

¹ Interdisciplinary Nanoscience Center, Aarhus University

av@inano.au.dk

Electrocatalytic oxygen evolution/reduction reaction (OER/ORR) are crucial for efficient energy storage and conversion in future energy systems [1]. However, the development of materials that are highly active, cost-efficient, and stable for OER/ORR remains an ongoing challenge. Heteroatom-doped carbon-based materials are interesting as a plethora of different coordination environments can be realized for transition metals inside a carbon matrix [2]. Among these, the M-N₄ coordination (where the metal is bound by 4 N atoms) has been predicted by density functional theory to exhibit superior performance for OER/ORR [3]. Porphyrins, which inherently possess an N₄ site capable of coordinating a metal atom, serve as an ideal model system for investigating the performance of different transition metals under OER/ORR conditions [4]. However, a previous study [5] demonstrated that singly adsorbed porphyrins degrade and desorb during OER at alkaline conditions.

To address the stability issue, we hypothesize that covalently binding the porphyrins will improve the stability of the formed porphyrin network compared to physisorbed porphyrins. Through an on-surface Ullmann coupling, we have formed a covalent monolayer of porphyrins on Au(111). Subsequently, we deposited the desired metal (e.g., Co, Ni, or a mix) into the N₄ coordination site of the porphyrins. The structures have been studied extensively using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy. Electrochemical (EC) measurements have been performed in our home-built UHV-compatible EC chamber to prevent contamination from the air [6]. By comparing EC measurements for different metals or metal combinations, we can identify reactivity trends and potential synergy effects arising from the presence of various metals. Importantly, the setup allows us to characterize the structures before and after EC and reveal if/how the M-porphyrin networks change chemically under different potentials.

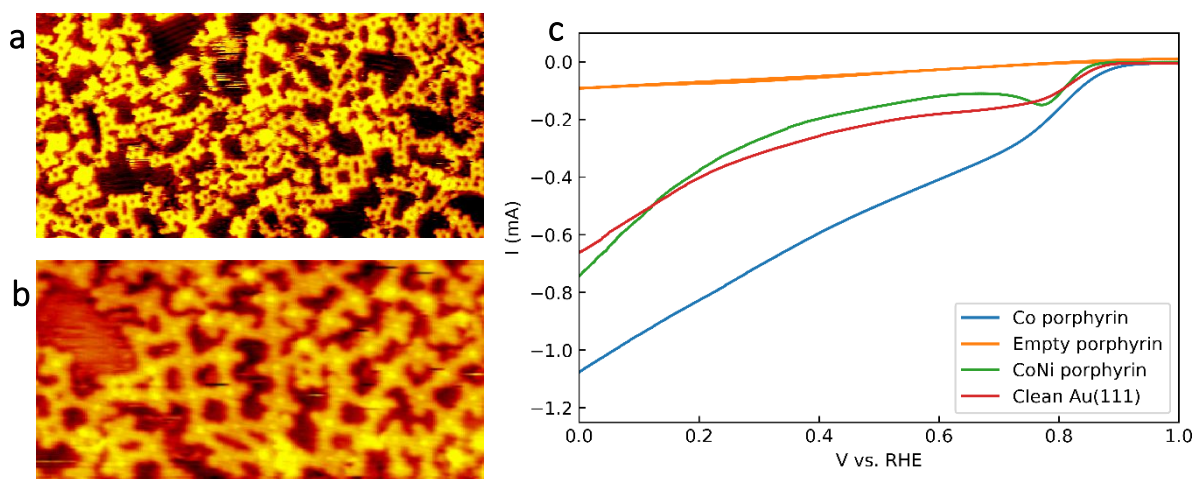


Fig. 1. STM images of **a)** empty porphyrin network (30 x 15 nm) and **b)** Co-porphyrin network (10 x 20 nm). **c)** Linear sweep voltammetry of different M-porphyrins. Scanning conditions: **a)** $I_t = 0.20$ nA, $V_t = 680$ mV. **b)** $I_t = 0.27$ nA, $V_t = 160$ mV.

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