Abstract:

Boosting efficiency of electrocatalytic water-splitting by magnetically induced heating

Co-supervisor 1: Prof. Dr. Matthias Driess, TU-Berlin

Co-supervisor 2: Prof. Dr. Bruno Chaudret, INSA Toulouse

The project aims at increasing efficiency of electrocatalytic water-splitting by magnetically induced heating of the electrodes locally in the immediate vicinity of deposited magnetic nanoparticles (NPs) under operating conditions of water-splitting. Suitable magnetically responsive as well as electrocatalytically active materials containing non-precious metal chalcogenides and pnictides are prepared by the molecular precursor approach. For example, strongly magnetically responsive iron phosphide NPs are accessible from a Fe_2P_3 precursor, which will be tested for magnetically induced heating during electrocatalysts. The as-prepared nanoparticles will be characterized by state-of-the-art techniques and then deposited on conducting electrode substrates. Catalytic performances for both oxygen (OER) and hydrogen evolution reaction (HER). Subsequently, the focus will be directed towards improving the efficiencies through locally hysteresis heating of electrodes under high-frequency alternating magnetic fields (AMF). This project is an international collaboration of UniSysCat PIs (Driess, Dau, Thomas, Strasser) with the Chaudret group at INSA Toulouse.

Extended description version of the project:

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1. Overall goal of the project

Over the last few years, we have synthesized several transition-metal-based nanoparticles with various morphologies that were highly active and durable for the electrocatalytic oxygen evolution reaction (OER), hydrogen evolution reaction (HER) as well as overall water-splitting (*Angew. Chem. Int. Ed.* **2018,** *57*, 11130). Interestingly, Chaudret and co-workers recently demonstrated a magnetic hyperthermia approach on nickel-coated iron carbide electrodes to improve the overall catalytic performance in alkaline water-splitting (*Nat. Energy.* **2018,** *3*, 1476). In this regard, the main research question of this project will be to synthesize magnetically responsive nanoparticles of various morphologies and application of such nanoparticles for bifunctional (OER and HER) water-splitting (both in alkaline and acidic) to significantly improve the current efficiencies through locally heating electrodes under high-frequency alternating magnetic fields (AMF). The proposed project aims at establishing a new collaborative partnership between UniSysCat (Driess) and INSA Toulouse (Chaudret)

2. State of the art

Electrocatalytic water-splitting has been considered as one of the most promising strategies to produce clean hydrogen fuel that involves HER at the cathode and OER at the anode. The highly efficient water electrolyzers are based on acidic proton-exchange membranes (PEMs) but contain precious metals on the electrode, hence impede mass commercialization. Alternatively, alkaline water electrolyzers (AWEs) operate at a low current density (mostly Ni-based electrodes) and display moderate energetic efficiency. Raising the operational temperature enhances the performances of PEM or AWE cell but also increases the energetic cost of the process and degradation of the cell components. *One of the key issues to address in the future is, whether water electrolyzers can be implemented near the equilibrium voltage at room temperature, which presently seems elusive in the current water electrolysis.* One of the best possible ways to achieve this goal is magnetic heating of electrodes locally in the immediate vicinity of deposited magnetic nanoparticles under operating conditions of water splitting, which is the main focus of the current project.

In previous work, the Driess group has synthesized numerous transition metal-based nanoparticles such as oxides (*J. Am. Chem. Soc.* **2014,** *136*, 17530) chalcogenides (*Angew. Chem. Int. Ed.* **2017,** *56*, 10506; *J. Am. Chem. Soc.* **2019,** *141*, 13306), phosphides (*Chem. Sci.* **2018,** *9*, 8590), alloys (*Angew. Chem. Int. Ed.* **2018,** *57*,15237), pnictides (*Angew. Chem. Int. Ed.* **2018,** *57*, 698), phosphates (*Adv. Funct. Mater.* **2019,** *29*, 1808632), phosphites (*Energy. Environ. Sci.* **2018,** *11*, 1287) as well as borophosphates (*Energy. Environ. Sci.* **2019,** 12, 988) with various morphology through molecular precursors as well as solid-state techniques that have shown exceptional activity and durability in alkaline water electrolysis. On the other hand, Chaudret and co-workers designed an innovative magnetic heating approach and activated Sabatier reaction (conversion of CO_2 into methane) as well as the Fischer–Tropsch (hydrogenation of CO) synthesis using various core-shell magnetic nanoparticles (*Angew. Chem. Int. Ed.* **2016,** *55*, 15894; Nano Lett. 2015, 15, 3241). This

concept was further extended to water electrolysis (*Nat. Energy.* **2018,** *3*, 1476) where a significant improvement in the performance of the electrodes was observed under alternating AMF. Thus, it is exciting to use magnetically induced heating approach (Chaudret, INSA) on various magnetically responsive nanoparticles that are already efficient for the reaction of OER and HER (Driess), to further increase the overall energetic efficiency.

3. Specific aims and how they may be reached.

The project proposal can be divided into two work packages (WP): **WP1** will aim at the controlled large scale synthesis of magnetically responsive nanoparticles of transition metal-based materials with protocols established in our laboratory. As a starting point, we will use high-purity and a well-defined molecular precursor that allows accurate control over the stoichiometry of the final material and maximizes the homogeneity of the material leading to a large number of hetero-linkages and benefits with respect to the surface and electronic properties. Starting from homo- and hetero-bimetallic ME_2M' (M or M' = Ni, Co, Fe, Mn; E = P, As, S, Se, Te) complexes developed by us recently (*Angew. Chem. Int. Ed.* ***2018,*** *57, 11130*), we will synthesize magnetic nanomaterials (Fig. 1) bearing ME_2M' moieties under hot-injection or solvothermal conditions and graft them directly on fluorine-doped tin oxide (FTO), indium tin oxide (ITO) as well as on conductive 3D nickel foam (NF) via electrophoretic deposition. The deposited electrodes will be directly investigated for individual half-reactions of OER and HER in alkaline and acidic media and subsequently in collaborations with the groups of Dau (FU) and Strasser (TU).

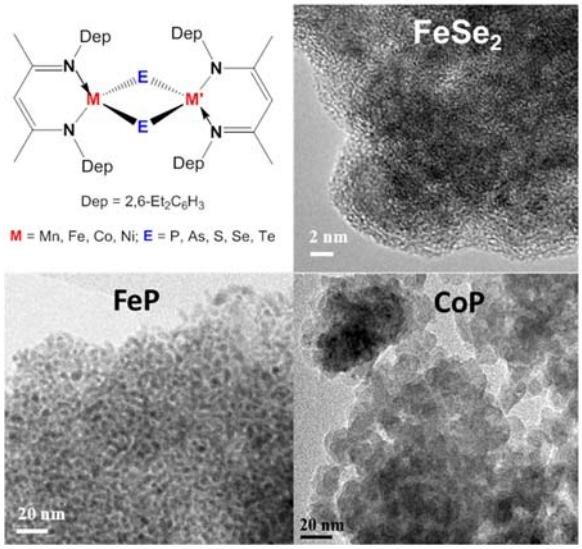

Fig. 1: Homo- and hetero-bimetallic complexes supported by β-diketimante ligands and the HR-TEM image of various nanoparticles

In **WP2,** the aforementioned magnetic nanoparticles will be used further to improve the efficiency of water splitting by magnetically induced heating (*Nat. Energy.* **2018,** *3*, 1476). In collaboration with the Chaudret group in Toulouse, the synthesized nanoparticles will be first deposited on the conducting substrate and the electrocatalytic water splitting will be conducted in the presence of AMF (Fig. 2) in acidic and alkaline media. The nanoparticles that display high heating capacity, as well as high adsorption rate, will be chosen such that particles could heat locally at various frequencies in order to achieve maximum output from the water-splitting cell.

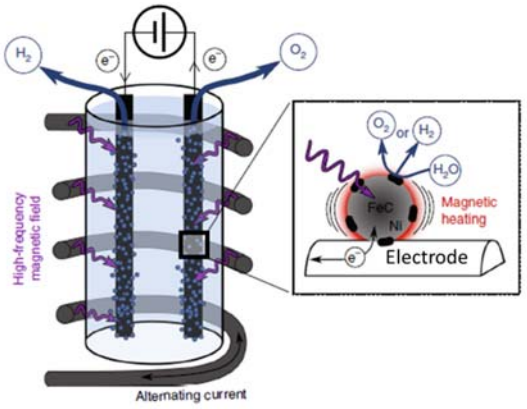

Fig. 2: Principle of water splitting activated by the local heating of magnetic nanoparticle (Ni@FeC in this case) by alternative magnetic field

Facilities: Driess group is well equipped with PXRD, ICP-AES, BET, SEM, TEM, and electrochemical set-ups. XPS will be carried out in collaboration with the Thomas group (TU). The water-splitting with at various AMF will be conducted in collaboration with Chaudret (INSA). *In-situ* X-ray set up will be developed at the KMC-3 beamline of the BESSY synchrotron in collaboration with the Dau group (FU).