2017 Helmholtz – OCPC – Programme

for the involvement of postdocs in bilateral collaboration projects

PART A

Title of the project: Single-Atom Gold Modification of NiFe Layered Double Hydroxide Films for High-Efficiency Oxygen Evolution Reaction

Helmholtz Centre and institute: Helmholtz-Zentrum Berlin für Materialien und Energie

Project leader: Prof. Dr. Kathrin Maria Aziz-Lange

Web-address: http://www.helmholtz-berlin.de/forschung/oe/ee/soft-x-ray/index_de.html

Description of the project (max. 1 page)**:**
Layered double hydroxides (LDHs) have attracted increasing attention in numerous research fields due to their intriguing physical and chemical properties. Especially, LDHs acting as oxygen evolution reaction (OER) electrocatalyts that can be applied for water splitting.[1] In spite of some recent advances in OER activity, it is still a long way to industrial applications, which require very large current densities at low overpotentials.
Recently, Kuo *et al.* demonstrated that doping MnO_x polymorphs with gold nanoparticles (AuNPs) can result in a strong enhancement of catalytic activity (~ 8.2 times) for the water oxidation reaction compared to the activity of pure α-MnO_2.[2a] Zhang *et al.* showed that Au can increase the turnover frequency (TOF) of MnO_x more than 10 times for the OER due to the unique local interaction between Au and MnO_x.[2b] However, gold is a costly material. So single-atom gold may be an ideal structure for precious gold minimization.
For the postdoc-project in bilateral collaboration, we propose to investigate single-atom Au modified NiFe LDH nanosheets that will be synthesized and characterized by the postdoc candidate at HZB. We want to correlate the OER performance of these materials to their electronic structure in order to understand e.g. differences in performance of single-atom gold versus AuNPs. Important questions in this context are, e.g.:

(1) Are the gold atoms properly dispersed across the NiFe LDHs?
(2) Is the Au bonding to Fe or Ni?
(3) Can the synthesis approach change the preference of bonding partner and how does this affect the performance of the material?

Our team has the experience and tools for the electronic structure investigations under *in*-situ/*operando* conditions of solar fuel materials. In order to obtain the structure and valence difference between single-atom gold and AuNPs modified NiFe LDHs Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Fine Structure (XANES) will be used on the Au L-edge, Ni and Fe K-edges using hard X-ray absorption spectroscopy (XAS) and on the Ni and Fe L-edges and the O K-edge using soft XAS at Bessy II. XAS is an element selective technique for determining the local structure and oxidation states of materials. XAS measurements at the K- and L-edges of Au, Ni, Fe and O will allow to identify structure and valence changes. Starting with ex-situ investigations in order to reveal the principle binding interaction between the single-atom gold/ AuNPs and the NiFe LDHs, we will proceed with *in-situ* and *operando* studies with our own cells[4] to monitor the changes induced by realistic working conditions and to reveal information about the catalytic active species.

Description of existing or sought Chinese collaboration partner institute (max. half page)**:**
Successful PhDs from the group of *Prof Bin Zhang, Tianjin University, PR China*[3] would be the ideal candidates for the postdocs in bilateral collaboration project since they are experienced in the synthesis of single-atom Au structures. In the group of *Prof B. Zhang* single-atom catalyst of gold supported on NiFe LDHs nanosheet arrays on a Ti mesh were already successfully prepared with the aid of hydrothermal synthesis and post-synthesis electrodeposition (see Fig.1). Fig. 1b shows a NiFe LDHs sheet TEM image. Fig. 1c show high-angle annular dark-field imaging (HAADF) image of single-atom Au on NiFe LDH. In Fig. 1c, single-atom gold can be clearly seen. They found that compared to AuNPs, the single-atom active sites predominantly showed a higher catalytic activity in water oxidation.

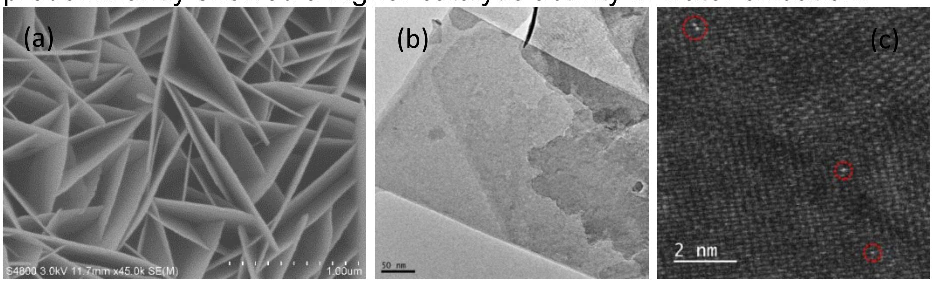

***Figure 1.** Morphology of single-atom Au/NiFe LDHs mesh films. (a)SEM, (b) TEM and (c) HAADF-STEM images of single-atom Au/NiFe LDHs. Note: the dotted circles in (c) show the single gold atoms.*

References
(1) (a) Cheng, F.; Chen, J. Chem. Soc. Rev. 2012, 41, 2172; (b) Lu, Z.; Xu, W.; Zhu, W.; Yang, Q.; Lei, X.; Liu, J.; Li, Y.; Sun, X.; Duan, X. Chem. Commun. 2014, 50, 6479.
(2) (a) Kuo, C. H.; Li, W.; Pahalagedara, L.; El-Sawy, A. M.; Kriz, D.; Genz, N.; Guild, C.; Ressler, T.; Suib, S. L.; He, J. Angew. Chem., Int. Ed. 2015, 54, 2345– 2350; (b) Zhang, H.; Lin, C.; Du, F.; Zhao, Y.; Gao, P.; Chen, H.; Jiao, Z.; Li, X.; Zhao, T.; Sun, Y. M. ACS Sustainable Chem. Eng. 2015, 3, 2049– 2057.
(3) Home page of Prof Bin Zhang's group: http://zbtju.weebly.com/members.html
(4) Schwanke,C.; Xi, L.; Lange, K. M. J. Synchrotron Rad. 2016, 23, 1390-1394.

Required qualification of the post-doc:
- PhD in Chemistry, Material Science or Physics.
- Experience with solution-based synthesis of noble metal modified electrocatalyst for oxygen evolution reaction and solar water splitting.
- Additional skills in TEM (HRTEM, SAED, EDS, STEM, EELS element), XPS and Raman.

PART B

Documents to be provided by the post-doc:
- Detailed description of the interest in joining the project (motivation letter)
- Curriculum vitae, copies of degrees
- List of publications
- 2 letters of recommendation

PART C

Additional requirements to be fulfilled by the post-doc:
- Max. age of 35 years
- PhD degree not older than 5 years
- Very good command of the English language
- Strong ability to work independently and in a team