

# Understanding the working mechanism of hematite-based water splitting photoanodes by operando X-ray absorption spectroscopy

A.S.M. Ismail<sup>1</sup>, Ivan G. Torregrosa<sup>1</sup>, Jeroen C. Vollenbroek<sup>2</sup>, Maarten Nachtegaal<sup>3</sup>, Mathieu Odijk<sup>2</sup>, Albert v.d. Berg<sup>2</sup>, Bert Weckhuysen<sup>1</sup>, F.M.F. de Groot<sup>1</sup>

<sup>1</sup>*Inorganic Chemistry and Catalysis Group, Utrecht University, the Netherlands*

<sup>2</sup>*BIOS LAB-ON-A-CHIP group, Twente University, the Netherlands*

<sup>3</sup>*In situ X-ray spectroscopy group. Paul Scherrer Institute 5232 Villigen – PSI Switzerland*

## Background

Photo-electrochemical (PEC) water oxidation on hematite-based photoanodes has attracted much scientific research attention in the last 20 years. Since hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has a suitable bandgap (2.1 eV), earth abundant and is stable throughout a wide range of pH. Although hematite has shown a potential to provide (theoretically) up to 15% solar-to-hydrogen efficiency, it was found that it could not reach this efficiency values under realistic water oxidation conditions [1]. This is mainly due to its sluggish oxygen evolution reaction (OER) kinetics and the mismatch between the light absorption depth (~400nm) and the minority carrier diffusion length (~10-20nm). Dopants and electrocatalysts have been found to improve the hematite OER performance by increasing the charge carrier concentration and reducing the onset potential respectively [2]. But how the presence of both the dopant and the electrocatalyst in one photoanodes system will affect its OER performance? And how the electronic and structural properties of iron in hematite changes during the water splitting process?

## Methods

In order to understand the electronic and structural changes of the hematite-based photoanodes, we carried out operando XAFS experiment during water splitting under different applied potentials and upon visible light illumination. A custom-built reactor was used where the hematite photoanodes were deposited on 1  $\mu$ m thick silicon nitride window where the hematite faces the electrolyte and the incident X-ray beam hits the sample from the back. The fluorescence detector was placed 45° relative to the incident beam.

## Results

Our goal from this work was to answer these questions by studying the effect of adding both titanium dopants and Ni(Fe)OOH electrocatalyst to hematite photoanodes. Photo-electrochemical characterization showed that adding titanium dopants or Ni(Fe)OOH electrocatalysts separately to hematite enhances its PEC activity, but combining both of them in hematite had a severe effect on its PEC performance. In order to further understand the nature of interaction between Ni(Fe)OOH and Ti dopants in hematite, we conducted operando X-ray absorption spectroscopy characterization on this system under PEC conditions in a specially designed reactor cell. Based on this study we found that both iron and nickel were clearly reduced during the water oxidation process. Further reduction of Fe and Ni took place in the samples that contained Ti more than the other samples. A shift in the intensity and energy position of both the XANES edge jump and pre-edge was also observed in these samples, which indicated a change in crystal structure of the system.

## Conclusion

First of all, we concluded that important structural and electronic changes take place in iron in hematite at the start of the photoelectrochemical process. We also found hints to the possibility of the interaction between the titanium dopants at the surface of hematite with Ni and Fe to form ilmenite species that have detrimental effects on the overall OER performance of the photoanode.

## References

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- [2] Lin, F.; Boettcher, S. W., *Nat. Mater.* **2013**, 13 (1), 81–86.