Correlative study of hematite-based photoanodes for solar water splitting by transmission electron and X-ray microscopies

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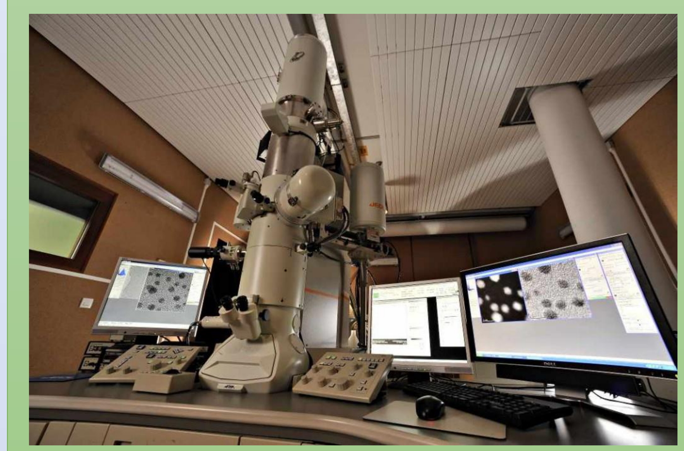
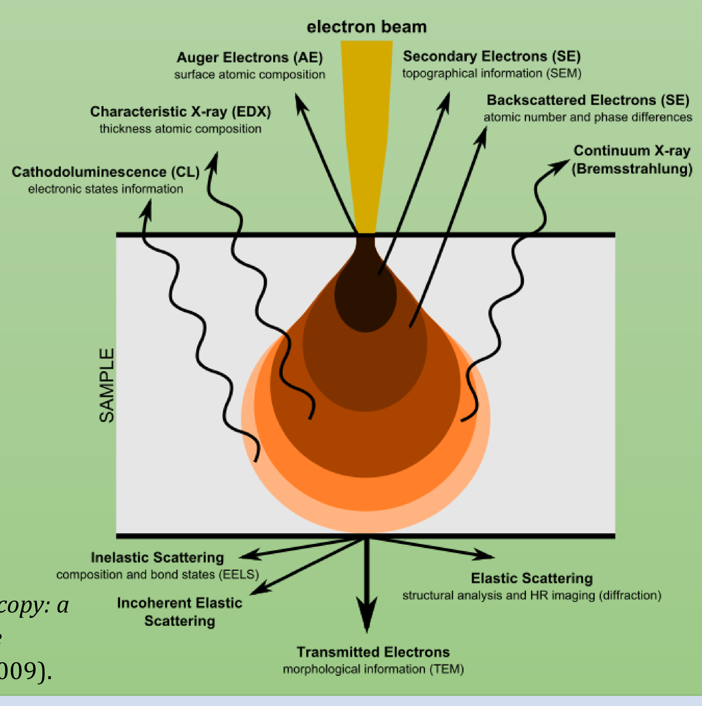
MOTIVATION

In the framework of renewable energies, use of hydrogen as an efficient energy storage is often discussed. Among the many candidates, Ti-doped hematite (Ti:α-Fe_2O_3) nanorods are extensively studied due to their high theoretical photocurrent, optimal band gap for solar light absorption, cost- and resource-efficiency.
For an extensive characterization of such materials, we have decided to correlate two complementary microscopic techniques, which, together with photoelectrochemical measurements, allow us to improve the synthesis of the material.

EXPERIMENTAL APPROACH

Transmission electron microscopy

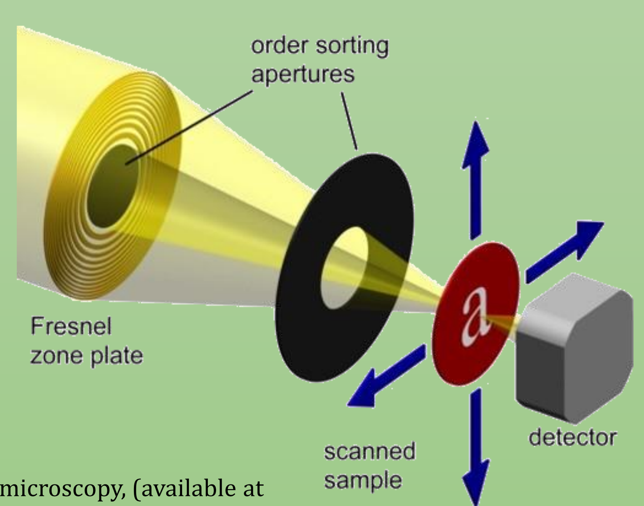




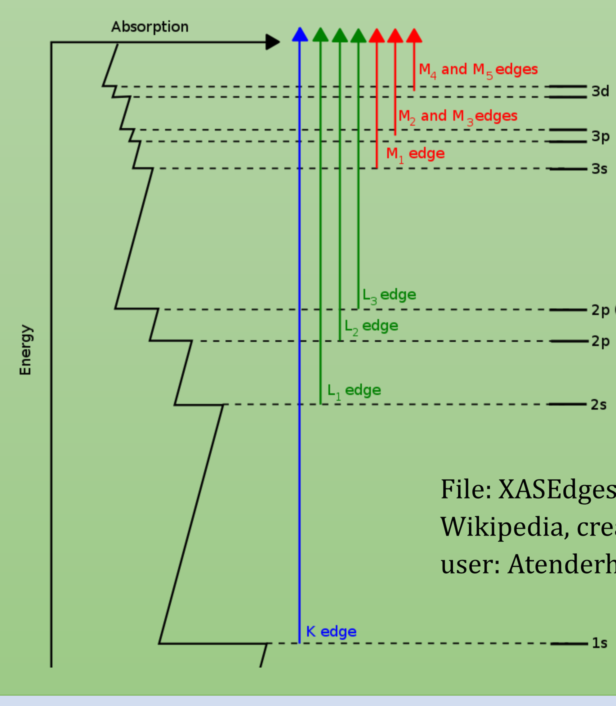
D. B. Williams, C. B. Carter, *Transmission electron microscopy: a textbook for materials science* (Springer, New York, 2. ed., 2009).

STRUCTURAL vs. **CHEMICAL** information

Scanning transmission X-ray microscopy



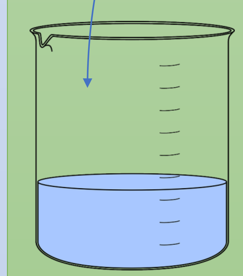
X-ray microscopy, (available at http://www.x-ray-optics.de/index.php/en/applications/imaging/microscopy).



File: XASEdges.svg on Wikipedia, created by user: Atenderholt

MATERIAL: SYNTHESIS & CHARACTERIZATION

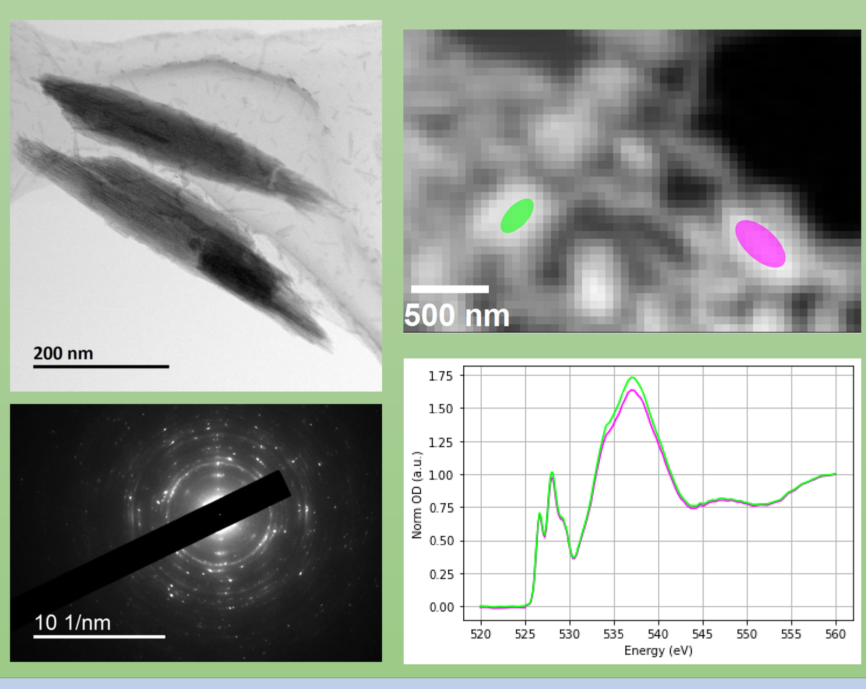
$FeCl_3$
$TiCl_3$
H_2O



95 °C
4 hours

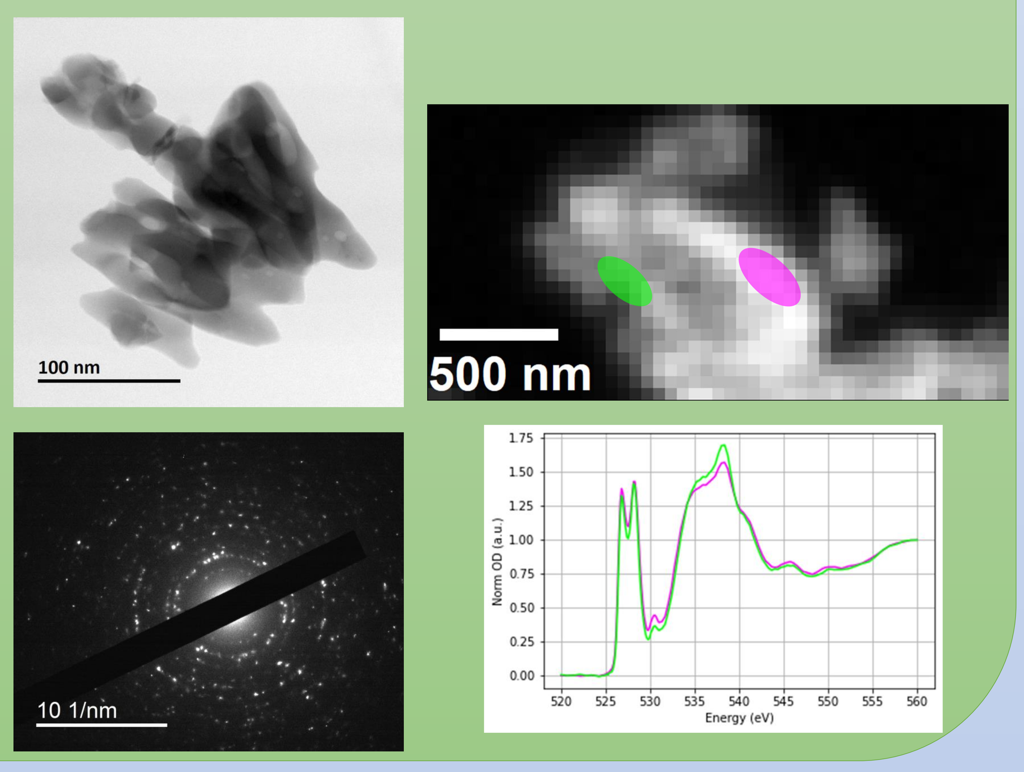
(1-x) $FeCl_3$ + x $TiCl_3$ + 2 H_2O → Ti:FeOOH + 3 HCl

TEM STXM

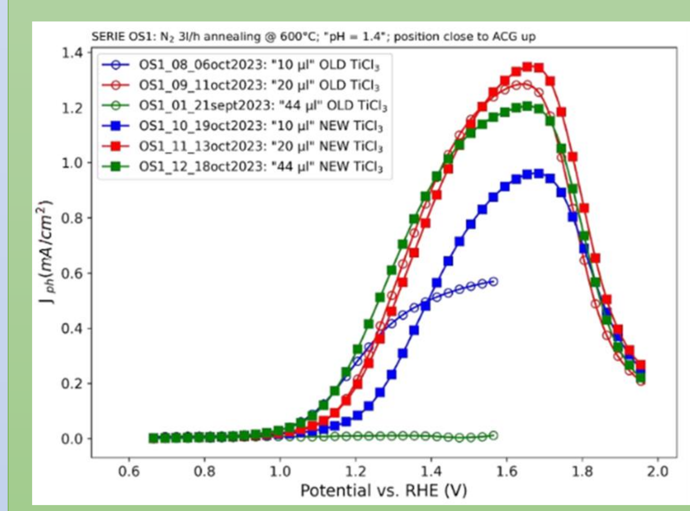


100% N_2
600 °C
4 hours

2 Ti:FeOOH → **Ti:Fe_2O_3** + H_2O



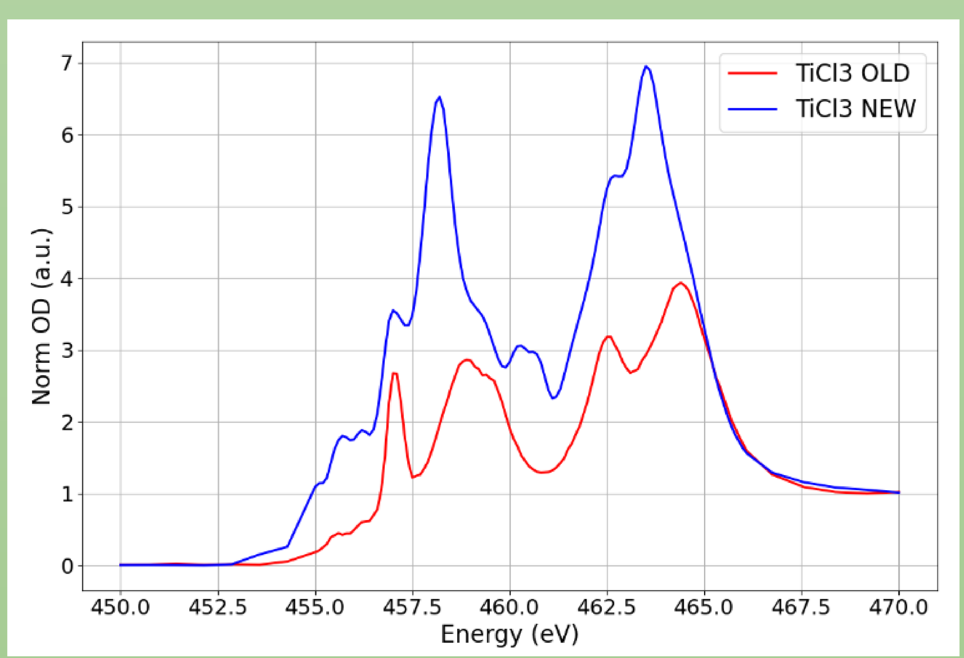
Photoelectrochemical properties



Aged precursor
Fresh precursor

RESULTS AND DISCUSSION

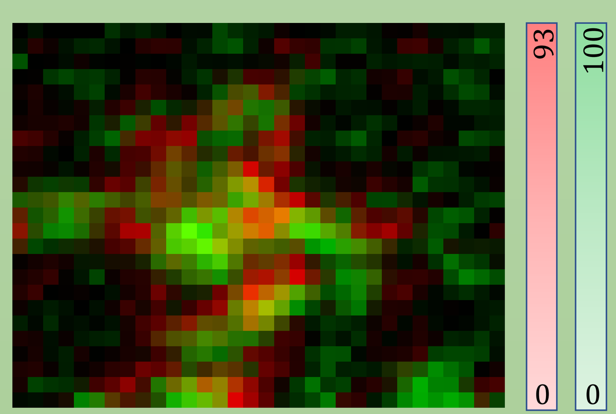
$TiCl_3$ precursor: chemical composition (STXM-XANES @Ti $L_{2,3}$-edge)



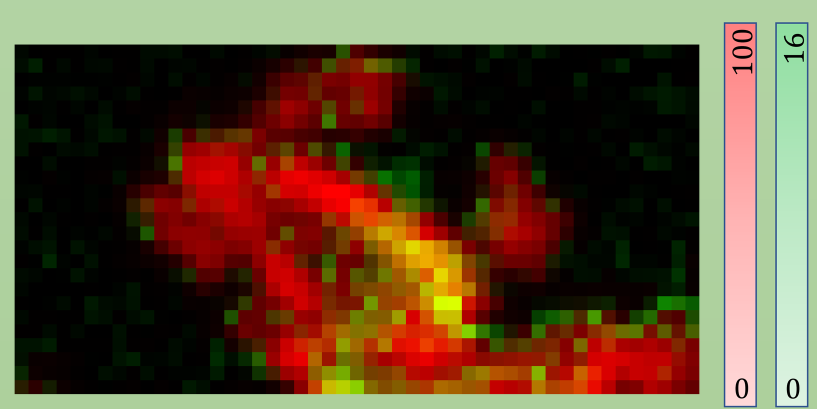
Aged precursor: XANES typical for TiO_2 ⇒ oxidated state Ti^{4+}

Fresh precursor: XANES correlates with multiplet calculations for Ti^{3+} in Oh symmetry

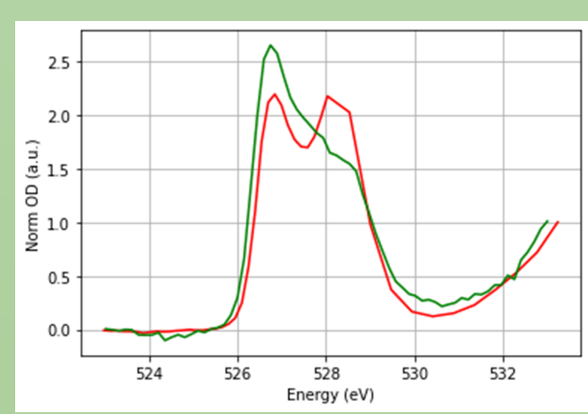
Ti:α-Fe_2O_3: comparing samples synthesized with aged vs. fresh $TiCl_3$ precursor



Using aged Ti precursor (S1)

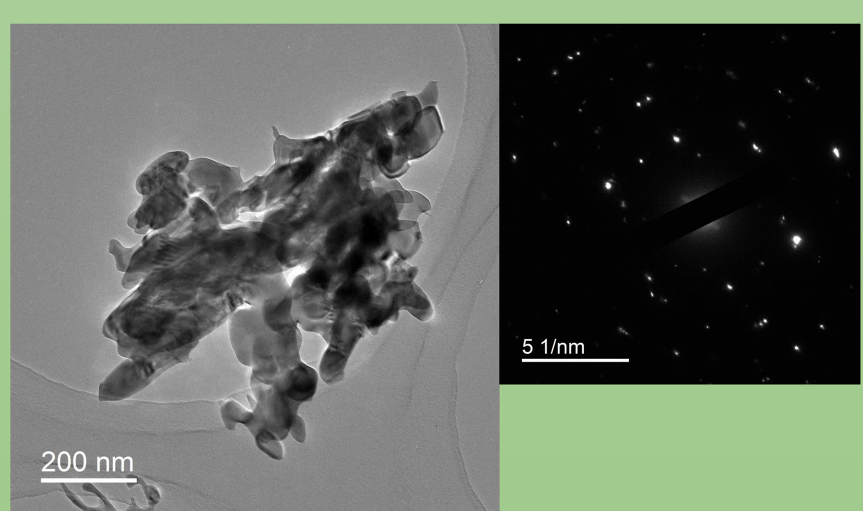


Using fresh Ti precursor (S2)

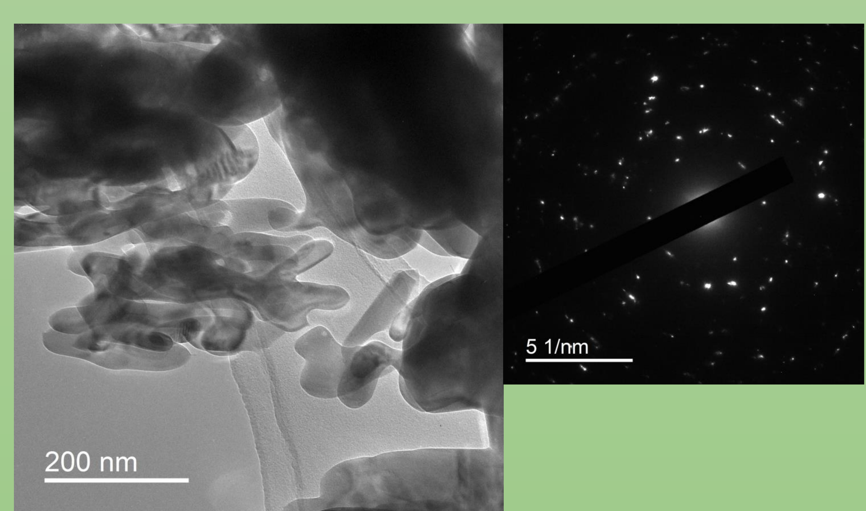


Reference spectra Extracted from S1

STXM @ O K-edge: the two samples are chemically different
S1: "partially reduced" hematite
S2: "normal" hematite

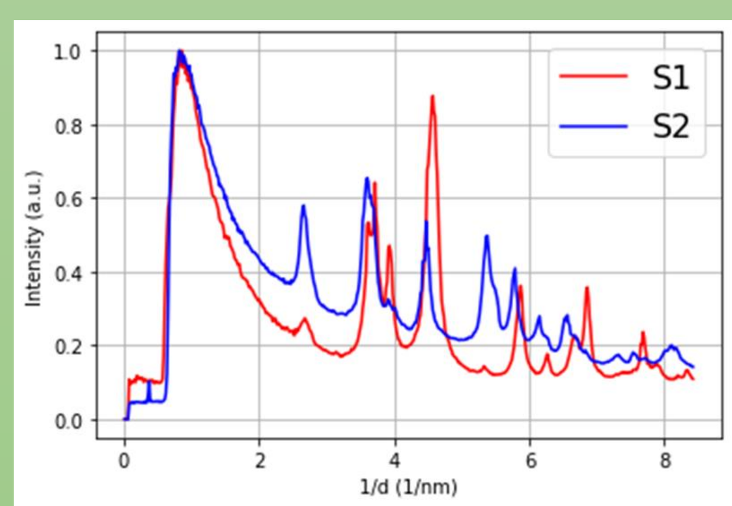


S1



S2

TEM: the two samples are structurally similar



SAED – radial plot: samples with aged vs. fresh precursor

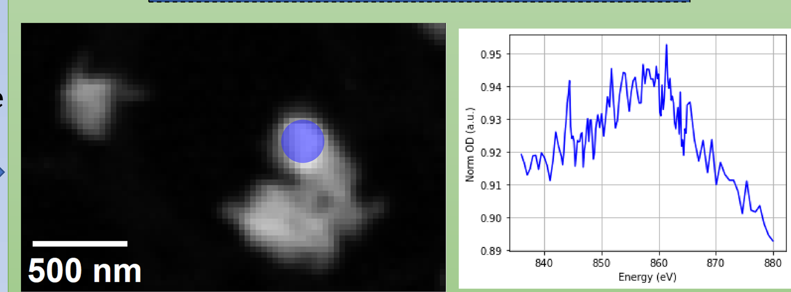
CONCLUSION AND PERSPECTIVES

Influence of precursor ageing on final material

- Aging of $TiCl_3$ precursor over time causes **oxidation** of Ti^{3+} to Ti^{4+}
- This leads to partial **reduction** of the **Fe^{3+}** cation to **Fe^{2+}** by charge compensation, yielding a chemically modified but structurally similar hematite material
- Such partially reduced samples perform poorly for solar water splitting

Future work

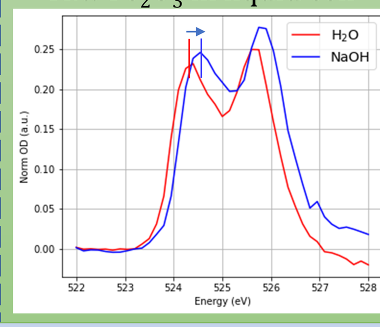
Ni/Zn cocatalysts



Amorphous Ni layer, likely homogeneous
To do: XPEEM !

In situ measurements

XAS spectra @ O K-edge of Ti:α-Fe_2O_3 in liquid cell



VB & CB Energy: +0.059 eV / pH @25°C (Nernst eq.)

+0.3 eV shift for sample in NaOH vs. in H_2O