Correlative *in situ* electron and X-ray microscopies study of hematite-based nanomaterials used for hydrogen production by sunlight

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Introduction

In the framework of hydrogen production as means for renewable energy storage, Ti-doped hematite (Ti:α-Fe_2O_3) nanorods used as photoanodes have received renewed interest, owing to their high theoretical photoelectrochemical activity, absorption spectrum compatible with sunlight, as well as the abundance of its constituents, allowing cost- and resource-efficient production of hydrogen by solar water splitting[1].

In previous work[2], a two-step synthesis for this material was developed: the aqueous chemical growth (ACG) deposition of Ti-doped akageneite (Ti:β-FeOOH) on a glass/FTO substrate using $FeCl_3$ and $TiCl_3$ precursors, followed by annealing in a controlled oxygen and nitrogen atmosphere to yield the final Ti-doped hematite photoelectrode structure.

Herein, we study the microstructural transformation of this nanostructure during the aforementioned annealing step by means of *in situ* gas phase transmission electron microscopy (TEM) correlated with synchrotron scanning transmission x-ray microscopy (STXM) analysis, in order to provide direct and real-time insight into its structural, morphological and chemical evolution.

Further work to understand the aqueous chemical growth step by similar correlative *in situ* techniques is also currently being carried out, to gain a deepened understanding throughout the complete synthesis process.

Materials and Methods

The *in situ* analysis was carried out by environmental TEM using a sealed MEMS-device-based holder inside the microscope, in which heating and a gas or liquid environment can be applied to the sample. The change in morphology and chemical composition was monitored in real time by scanning transmission electron microscopy (STEM) imaging and energy-dispersive X-ray spectroscopy (EDS) mapping, and structural information was gained by electron diffraction. Additionally, the same sample was analyzed by STXM at the HERMES beamline (Synchrotron SOLEIL), where information on the spatial distribution of its electronic structure and composition was obtained.

Results and Discussion

Notably, the formation of various morphological and structural features as a function of temperature and time was observed (shown in Figure 1), which can be linked to a change in the electronic properties, possibly acting as charge recombination sites[3]. Furthermore, clusters of pseudo-brookite (Fe_2TiO_5) were found by spectro-ptychography and high-resolution TEM (Figure 2), which are beneficial to the photoelectrochemical activity by improving charge separation at the interface[4]. It was evidenced that these clusters are found only after annealing in an oxygen-deprived atmosphere, therefore allowing fine-tuning of the reaction conditions to improve the photoelectrochemical activity.

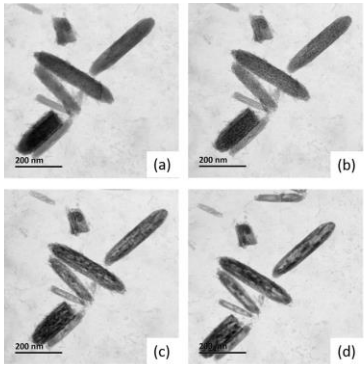

Figure 1. *In situ* BF (bright-field)-STEM images of Ti:β-FeOOH particles during annealing at (a) 200 °C, (b) 400 °C, (c) 600°C, (d) 800 °C under N_2.

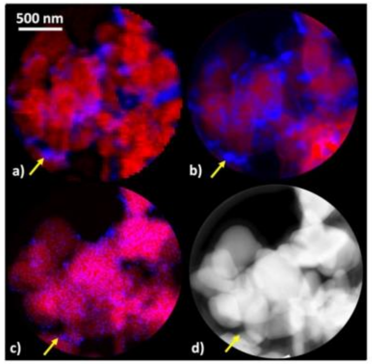

Figure 2. (a) STXM, (b) spectro-ptychography, (c) STEM-EDS map, (d) corresponding STEM-HAADF (high-angle annular dark-field) image of nitrogen-annealed photoanodes. In red, bulk Ti:Fe_2O_3, in blue, pseudo-brookite clusters[4].

Significance

This work provides key information on the dynamics of the genesis and transformation of the studied material, and creates a link between the theoretical insight and the activity and performance of the photoelectrode, with the ultimate goal of increasing the efficiency of solar water splitting for hydrogen production.

References

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