Investigation of optoelectronic properties of photoelectrode surfaces with high spatial resolution by Atomic Force Microscopy (AFM) for photoelectrochemical (PEC) water splitting and solar fuel production application

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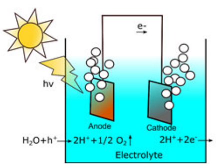
1- Motivation

- In order to protect the surface of photocatalytic semiconductors from degradation, a thin coating of Titanium dioxide (TiO_2) is often deposited by atomic layer deposition (ALD). In addition to their protecting function, the optoelectronic properties of these thin films play a crucial role, since they significantly affect the overall performance of the device.
- AFM methods constitute a powerful tool to investigate photo-induced charge separation, charge transport and recombination mechanisms on photoelectrode surfaces with nanometer resolution.
- This information complements bulk characterization methods by providing deep insights into the operation mechanisms at the nanoscale, enabling us to engineer promising material systems and devices with enhanced macroscopic performance and efficiency.

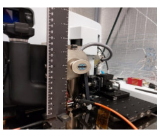
2- Application



- Photoelectrochemical cells (PECs) hold great promise as an environmentally friendly method of converting sunlight into hydrogen through water splitting.
- The development and design of macroscopically efficient and stable PEC devices can significantly benefit from powerful characterization methods at nanoscale, in order to reveal underlying properties and mechanisms, which considerably affect the overall performance of the device.

3- Experimental Setup

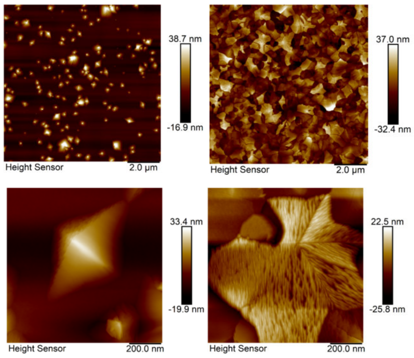
Bruker Dimension Icon SPM: AFM (contact, tapping, PeakForce Tapping), STM, KPFM, CAFM/TUNA, EC-AFM, nanoSECM.



Custom made setup for variable angle and height side illumination.

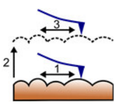
4- Results

4.1- High resolution topography

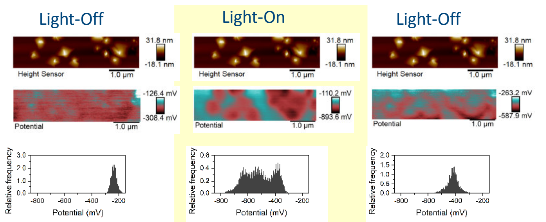


High resolution topography maps of TiO_2 thin films grown by thermally activated atomic layer deposition (ALD) at 220 °C (left) with mixed phase morphology (crystalline and amorphous) and 240 °C (right) with fully crystalline microstructure.

4.2- Using PF-KPFM to measure surface potential in dark and under illumination to study carrier dynamics

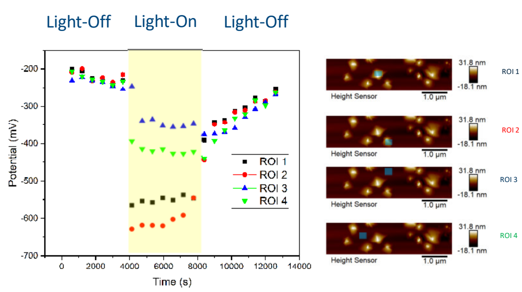


PF-KPFM principle to measure local surface potential along with the topography in dual-pass

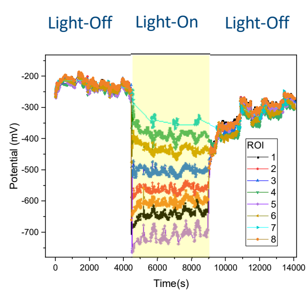


Middle row: surface potential maps of mixed phase ALD TiO_2 in the dark (left), after turning the (365 nm) illumination ON (center) and just after turning the illumination OFF (right). The bottom row shows the histograms for the surface potential data, the top row shows the corresponding topography maps.

4.3- Manual extraction of surface potential transients from a series of KPFM measurements performed in the dark and under illumination

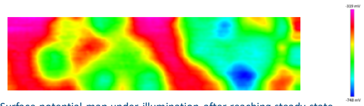


1) Manually defining different regions of interest (ROIs) within crystallites and amorphous matrix
2) Extracting the averages of the surface potential of these regions
3) Following the evolution of surface potential over the time for these ROIS.

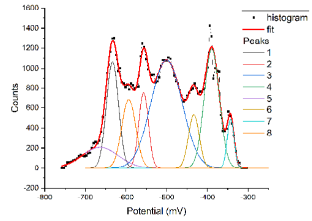


3) CPD transients with increased resolution relative to manually extracted transients.

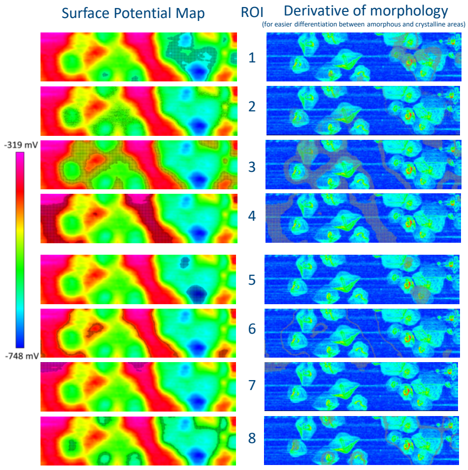
4.4- Automated extraction of surface potential transients from a series of KPFM measurements performed in the dark and under illumination



1) Surface potential map under illumination after reaching steady state condition as reference (measured potential maps were Gaussian smoothed with sigma = 20 nm / 2 pixels)



2) Extracted histogram of last surface potential measurement under illumination, identifying 8 distinct peaks, using these ranges as criterion to generate masks to mark regions (ROIs) corresponding to the peaks on the topography map.



Maps of the surface and corresponding maps of the derivative of the morphology for the different ROIs belonging to the peaks in the histogram.

5- Conclusion

5- Conclusion: There is a close and strong correlation between topography and optoelectronic properties, this paves the way towards discovering and developing of new promising materials for efficient stable PEC devices.

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