Electrodeposited zinc oxide nanorods covered with atomic-layer-deposited hematite film

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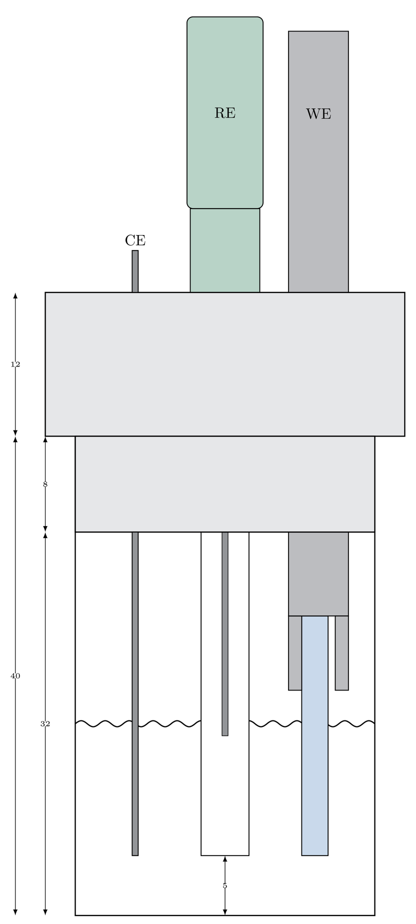
Electrochemical deposition of ZnO

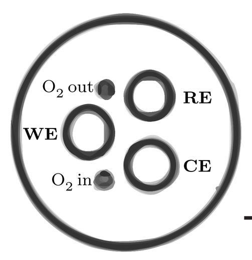
The working electrode is kept at a potential negative to the reduction potential of O_2, which causes oxygen gas near the electrode to be reduced to hydroxide ions. The hydroxide ions react with the zinc ions and forms zinc hydroxide, zinc oxyhydroxide or zinc oxide (depending on temperature).

$$\tfrac{1}{2}\mathrm{O_2} + \mathrm{H_2O} + 2\,\mathrm{e^-} \leftrightarrow 2\,\mathrm{OH^-} \qquad (\mathrm{E^\circ} = 0.40\,\mathrm{V})$$

$$\mathrm{Zn^{2+}} + 2\,\mathrm{OH^-} \rightarrow \mathrm{ZnO} + \mathrm{H_2O}$$



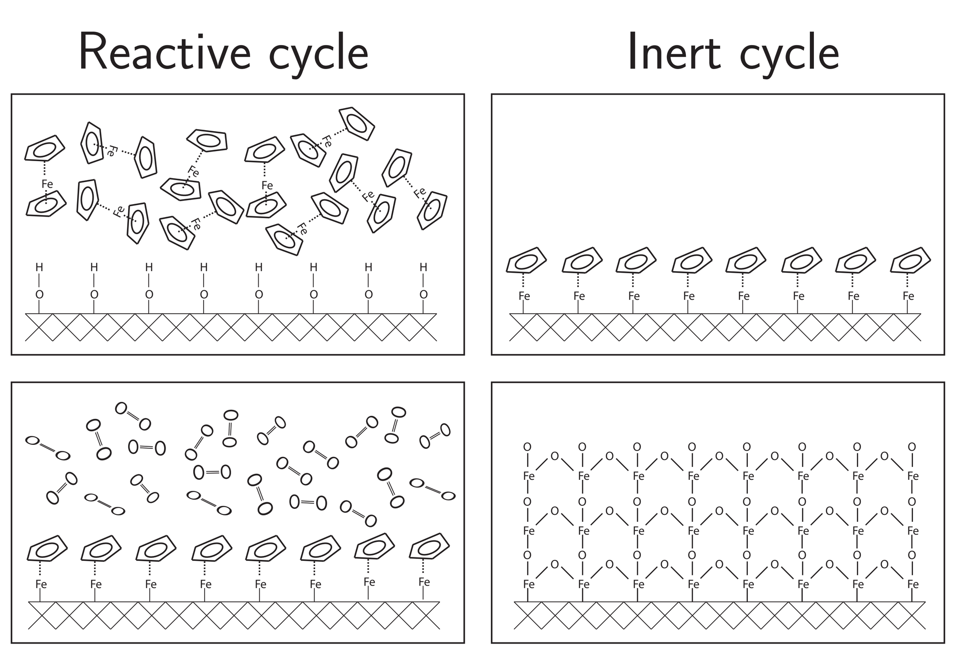
The oxygen is supplied by oxygen-bubbling into the headspace compartment (electrolyte solution is saturated prior to cell on).



The small schematic (above) shows the configuration of the cell as seen from above. The large schematic (left) shows the electrodeposition cell seen from the side (drawn to scale).

Cathodic deposition at -0.7 V vs. Ag/AgCl for 90 min with an initial pulse at -1.3 V vs. Ag/AgCl for 0.1 s, 0.5 s or 1.0 s. Electrolyte: 0.1 mmol dm^{-3} $ZnCl_2$(aq) and 0.1 mol dm^{-3} KCl(aq).

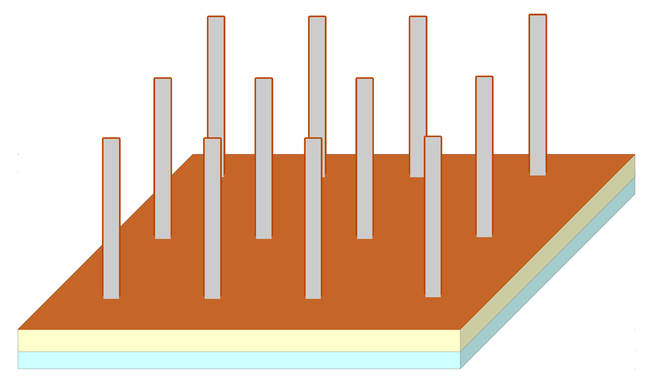
Atomic-layer-deposition of hematite



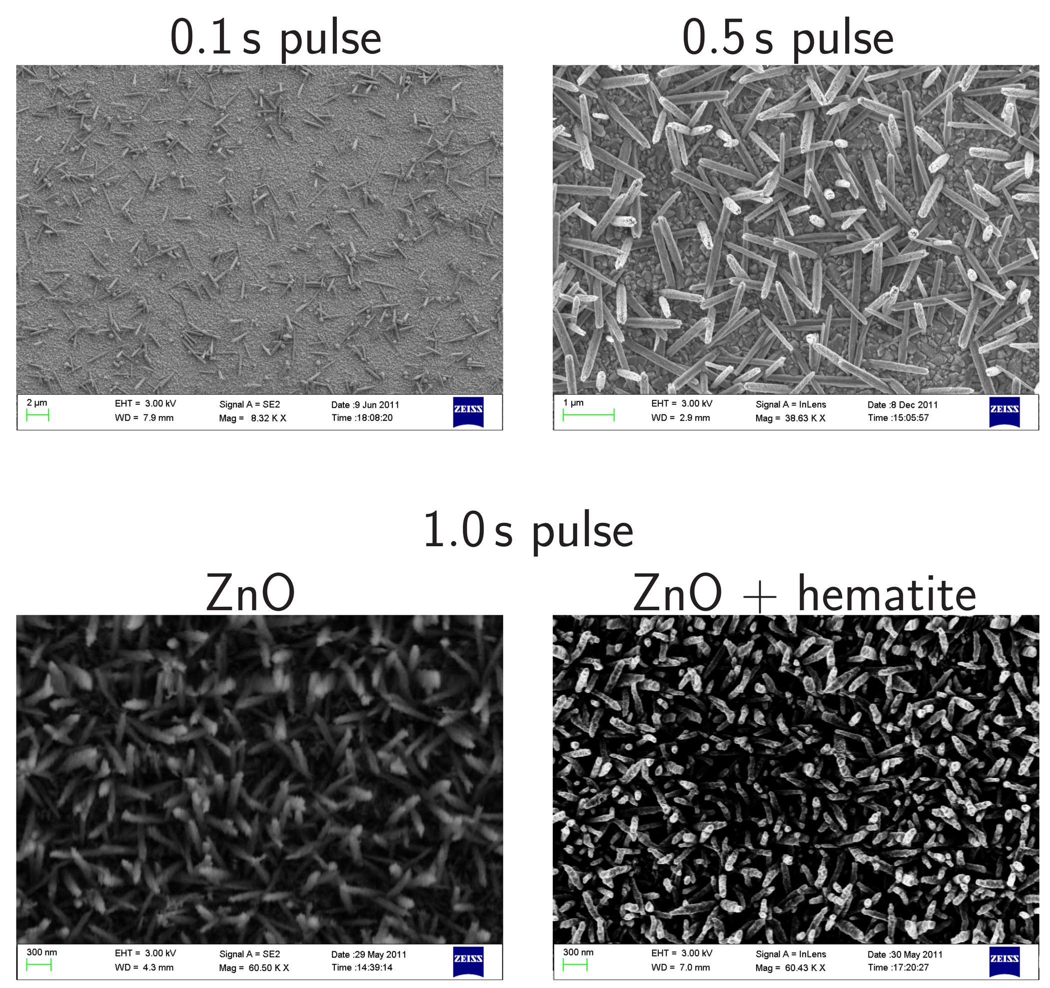
- Ferrocene precursor, chamber at 450 °C
- Hematite deposited using 35, 50, 62, 75, 87, or 100 cycles.

Deposition on flat reference samples show a hematite film thickness between 2 nm to 20 nm.

SEM and sample morphology

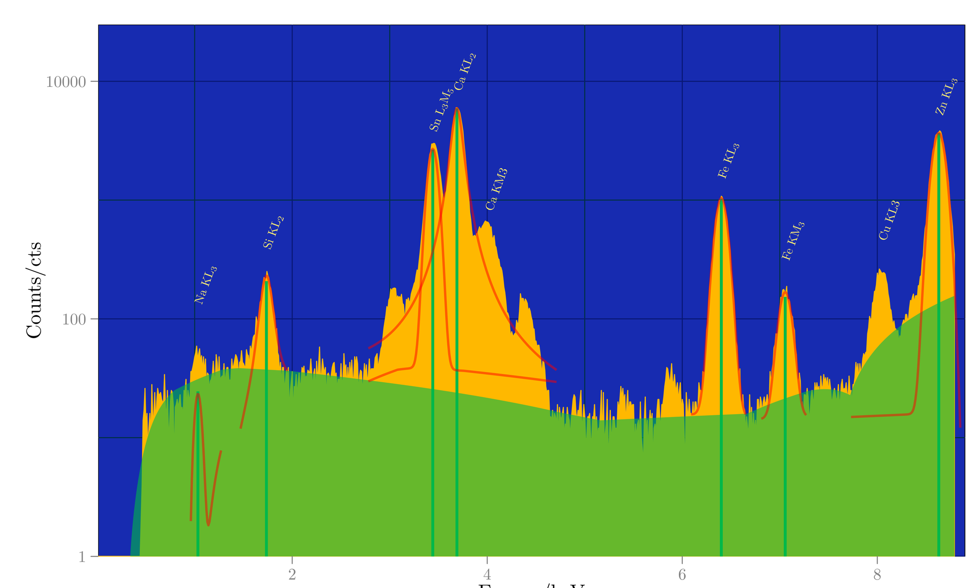


Drawing to the left shows a schematic of sample morphology: TEC7-glass substrate (FTO, yellow, on sodalime glass, blue), with vertical ZnO nanorods (between 1 µm to 2 µm long, and 0.2 µm to 0.4 µm thick), all covered with a relatively thin layer of hematite, red.



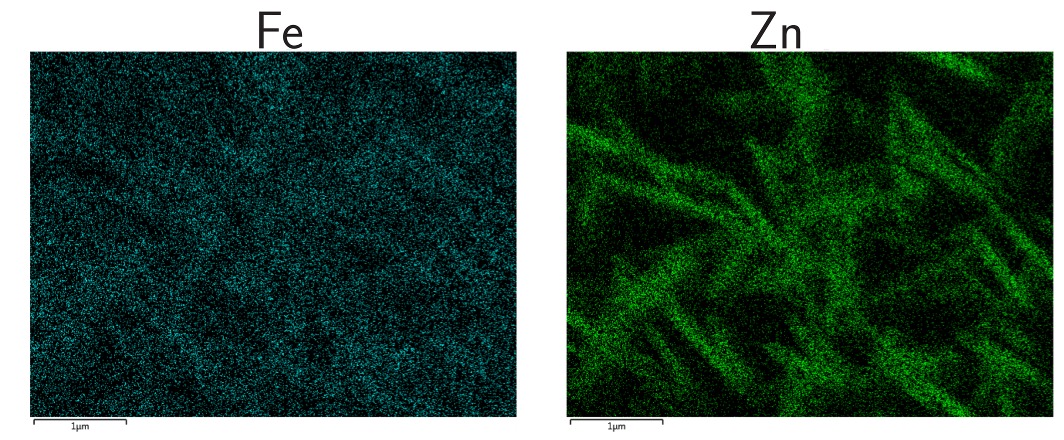
X-ray fluorescence spectroscopy

Experimental spectra (yellow) with fitted background (green), fitted kernels (red), and transition labels.

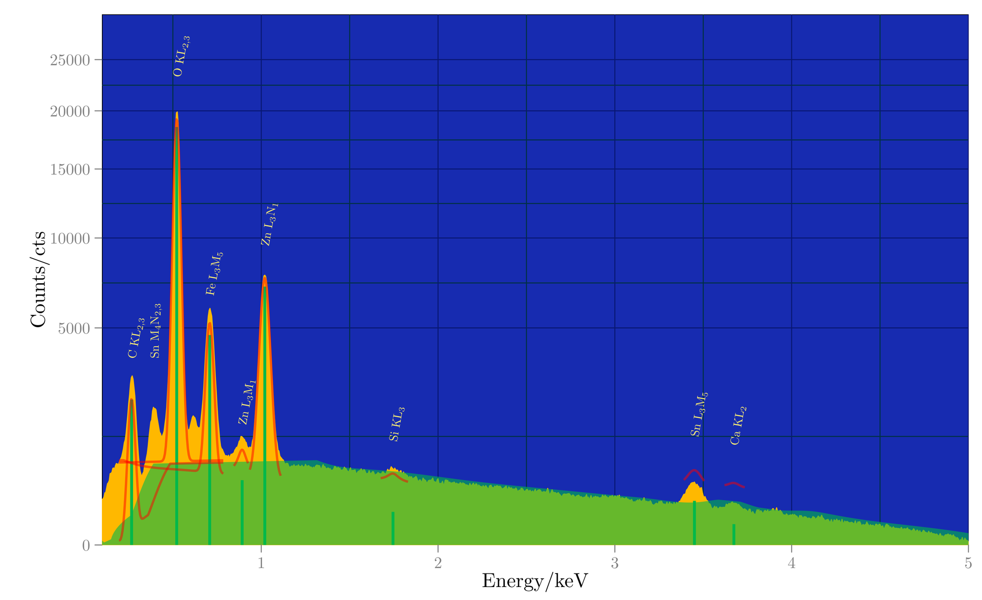


- XRF confirms the presence of tin (substrate), zinc (nanorods), and iron (hematite-layer).
- Calcium and sodium are common ingredients in sodalime glass.
- Copper and silicon are possibly contaminants in the sample.

Energy-dispersive spectroscopy

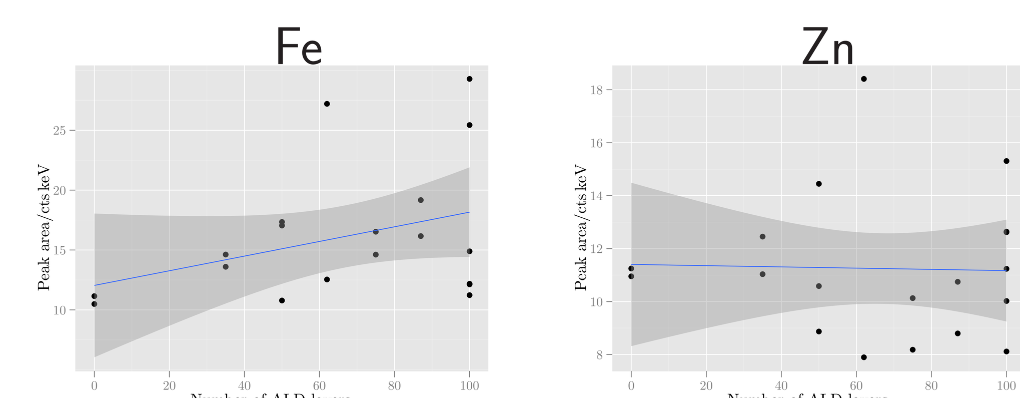


X-ray mapping of a sample at the micro-scale highlights the different distribution (in the plane) of the Fe_2O_3 and ZnO phases. The iron-containing phase is spread evenly across the sample, whereas the zinc oxide is localized in rod-like structures.



- EDS corroborates the XRF results.
- The lower intensities of the calcium, sodium, and silicon peaks suggest that these elements are not present at high concentrations in the surface layer of the sample.

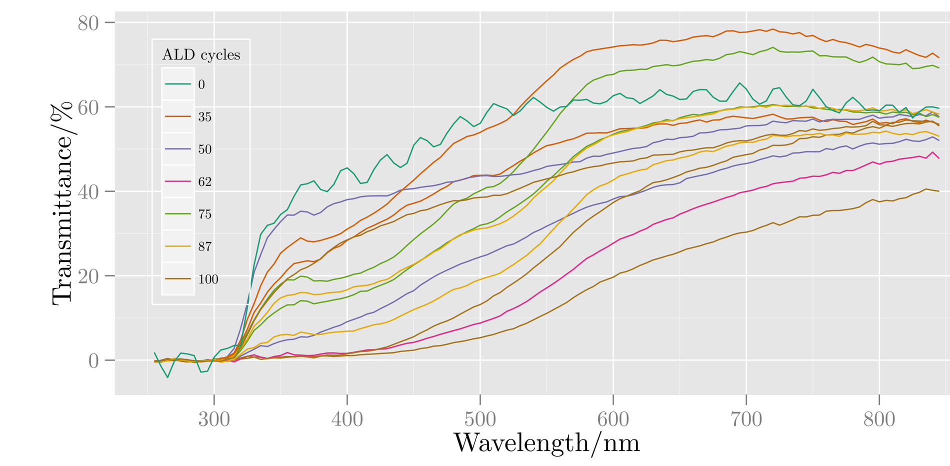
Amount of Fe correlates with ALD cycles

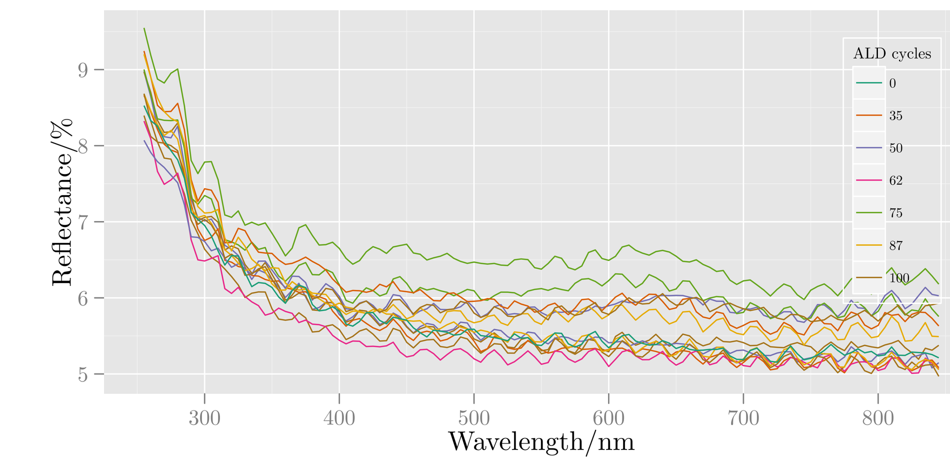


Amount of Fe correlates (albeit weakly) with the XRF peak area of the strongest iron transition. In contrast, the amount of Zn does not correlate at all with the number of ALD cycles (as expected).

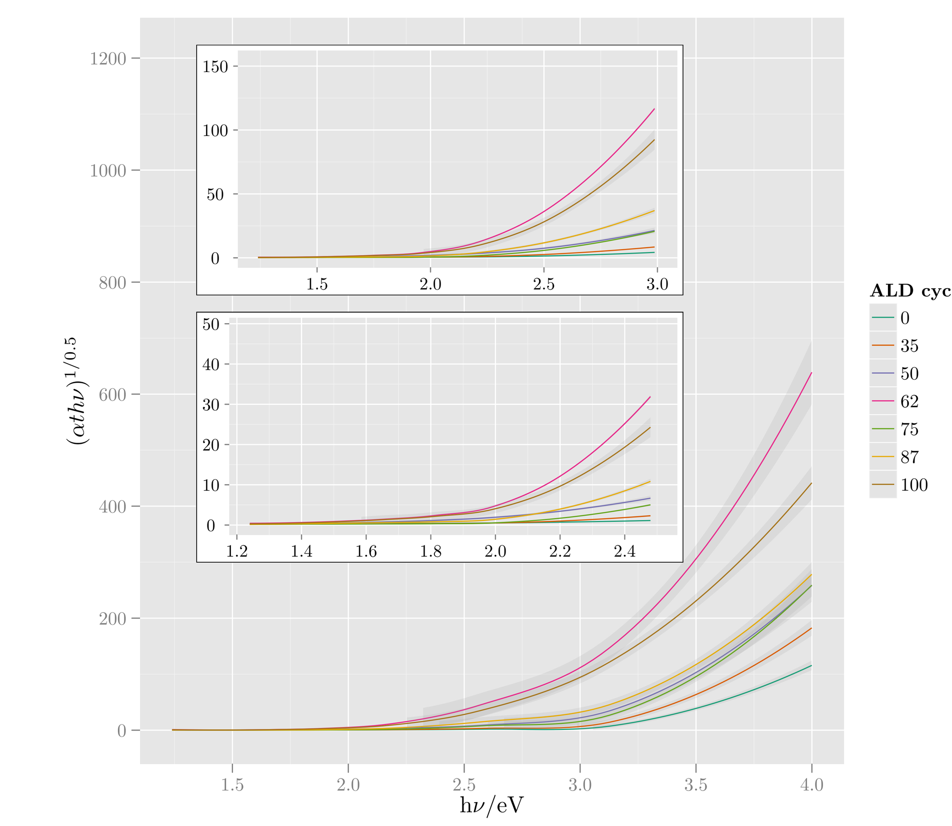
We observed the same trend using Raman spectroscopy, but only for flat (reference) samples. The Raman signal from hematite deposited on nanorod samples was too weak for quantification.

UV/Vis spectroscopy

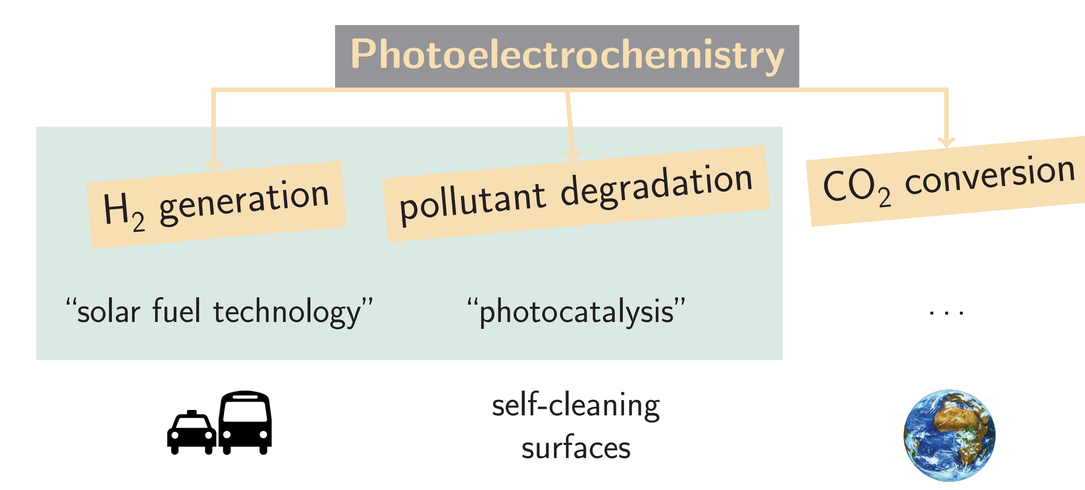




In the ≤ 500 nm region the transmittance decreases for increasing ALD cycles, except at 62 cycles, which shows an unexpected low transmittance at all wavelengths.



Photoelectrochemical applications



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