In-situ nanoscale characterization of cyclic reduction and reoxidation of CeO_x islands on Cu(111)

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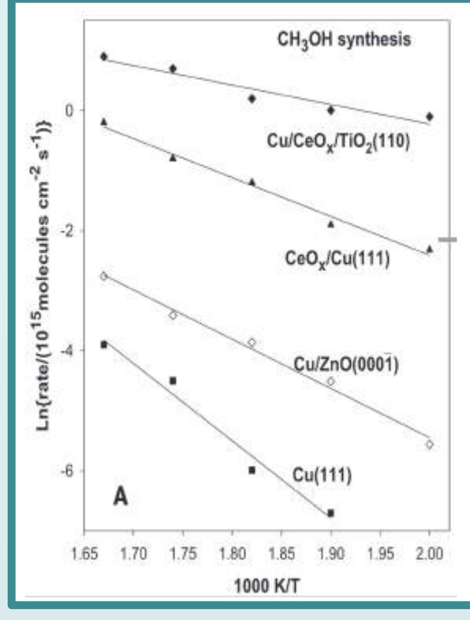
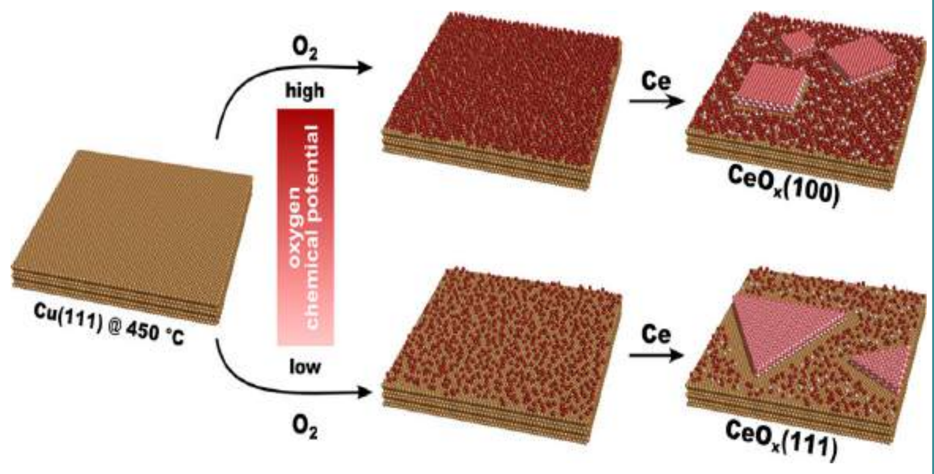
Introduction



- Methanol is a prototypical synthetic fuel.
- CeO_x/Cu(111) is a highly active catalyst for CO_2 conversion to methanol (left) [1].
- CeO_x(100) islands may also be active [2] ☞ controlled side-by-side growth [3].
- H_2 exposure leads to Ce^{3+} sites, which can activate CO_2 molecules and are essential for methanol synthesis [1,4].



Experimental

1. **Ceria island growth**:
   - Substrate: Cu(111)
   - T = 470 °C, $p(O_2) = 2\cdot10^{-6}$ mbar
   - evaporation of metallic Ce
   - I(V)-LEEM, XAS-PEEM **@Nanospectroscopy beamline Elettra**
2. **Treatments (550 °C)**
   - Reduction: $p(H_2) \leq 1\cdot10^{-5}$ mbar, H_2 dose: 179 kL
   - Reoxidation: $p(CO_2) \leq 1\cdot10^{-4}$ mbar, CO_2 dose: 145 kL
   - 2nd redox cycle: $p(H_2, CO_2) = 1\cdot10^{-5}$ mbar, H_2^{max} dose: 14.4 kL, CO_2^{max} dose: 28.4 kL

In situ growth of CeO_2/Cu(111)

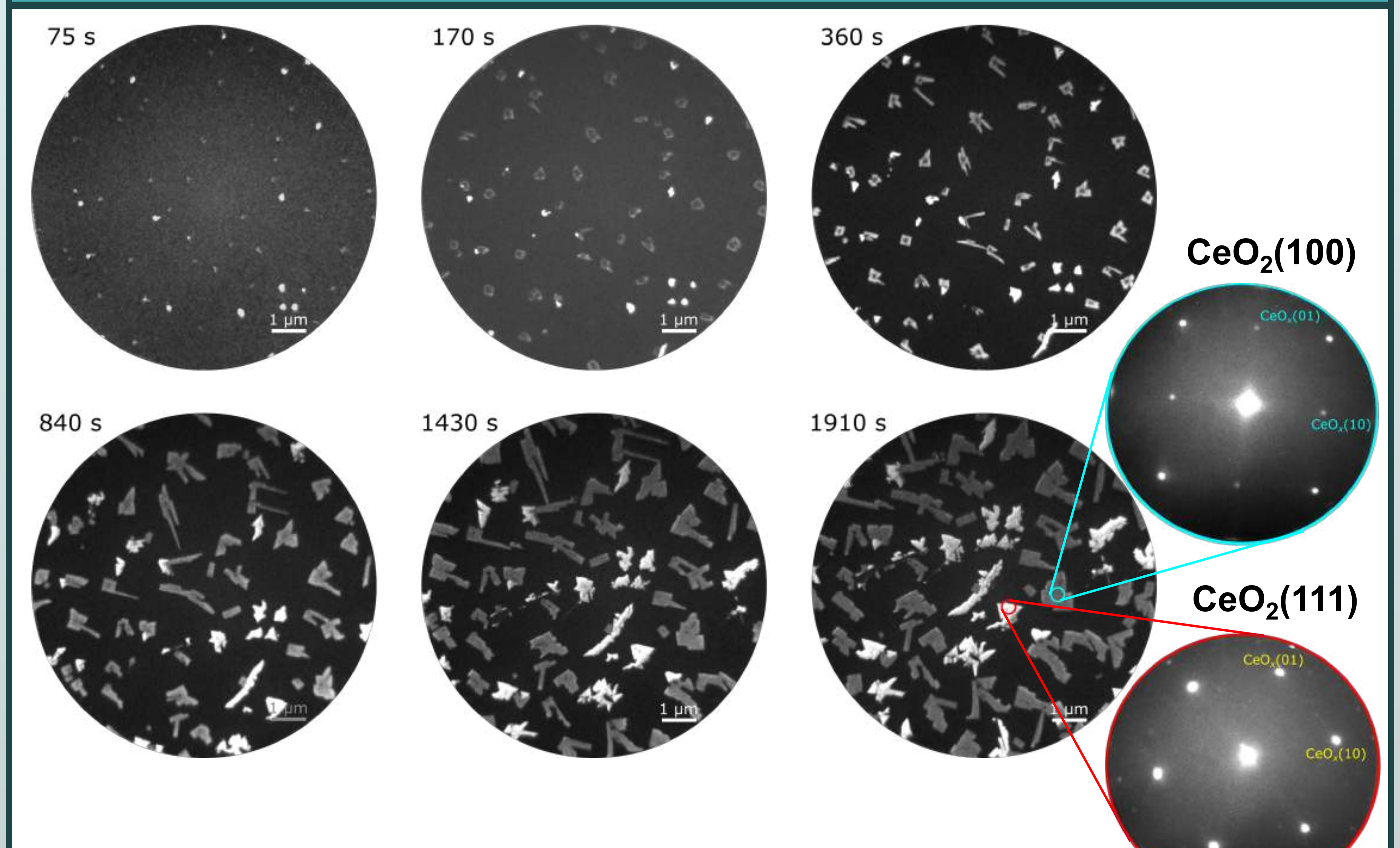


Figure 1: LEEM image sequence (8 eV) during cerium oxide growth [3]. LEED images taken at 200 °C (25 eV) after growth.

Figure 2: XAS-PEEM spectra for reduction with H_2 (left, from [5]), during reduction with H_2 (middle), and during reoxidation with CO_2 (right).

Figure 3: I(V)-LEEM curves during reduction with H_2 (left) and reoxidation with CO_2 (right).

Reduction and reoxidation: XAS-PEEM @ Ce $M_{4,5}$ edge

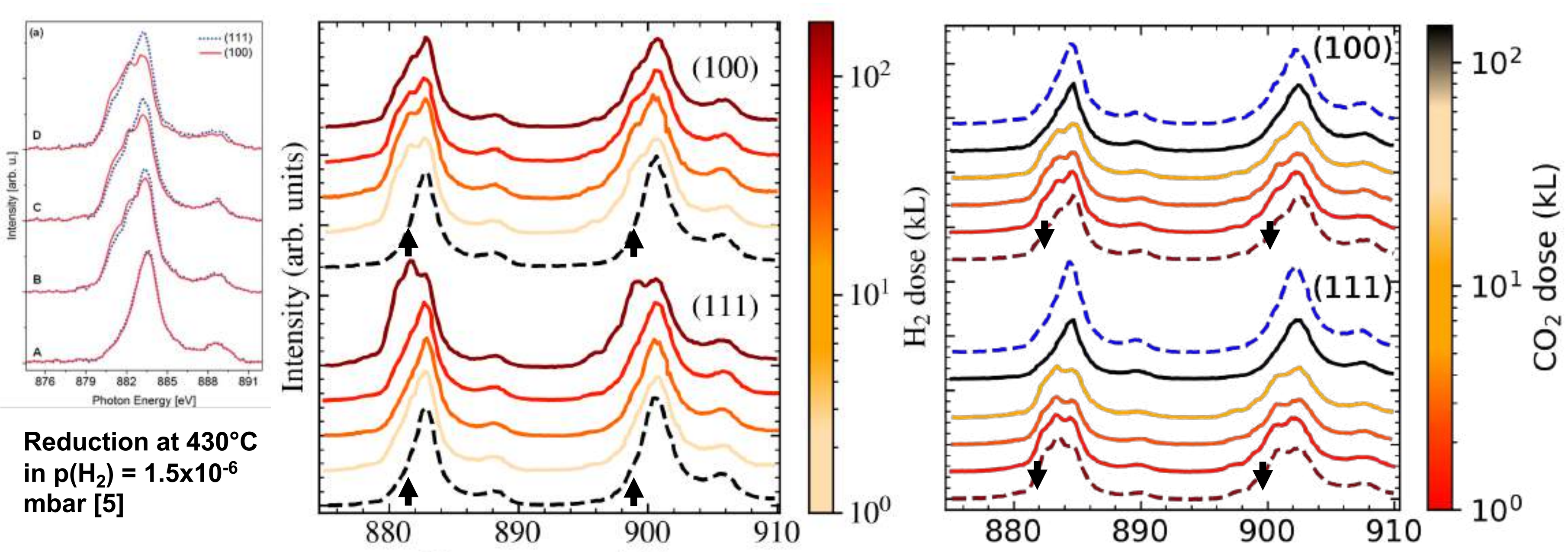


Figure 2

Reduction and reoxidation: I(V)-LEEM of single islands

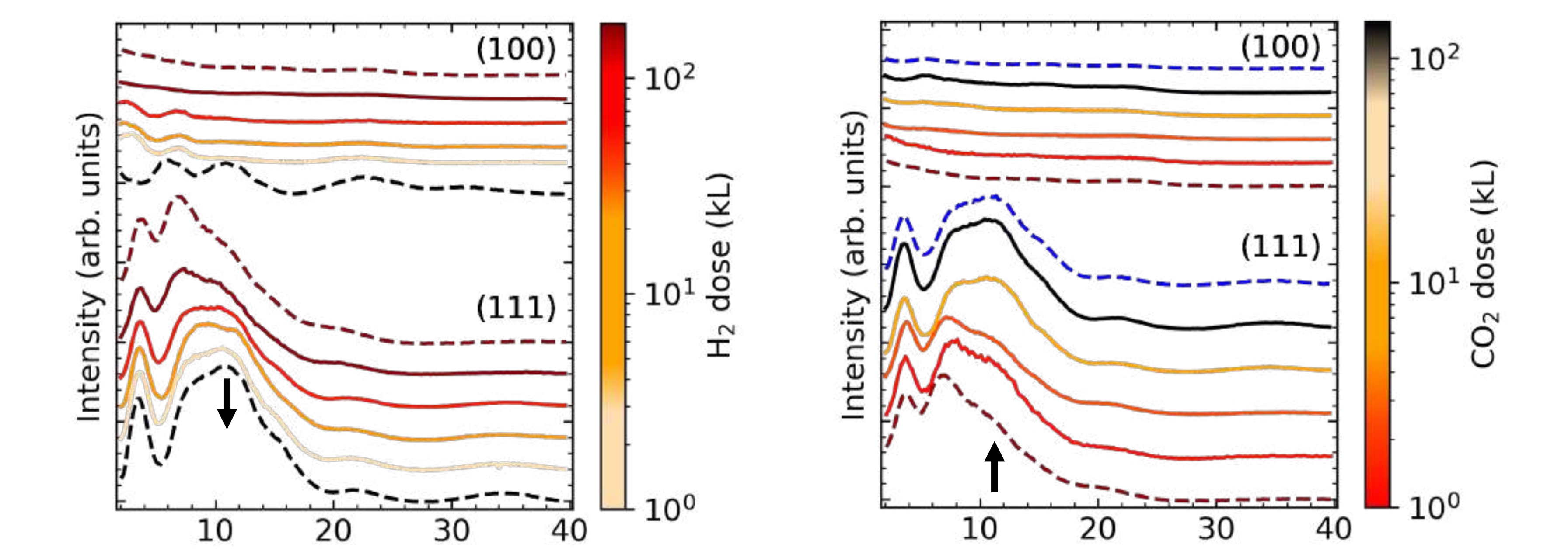


Figure 3

Dynamic I(V)-LEEM with pixel-wise analysis: 2nd redox cycle of CeO_2(111)

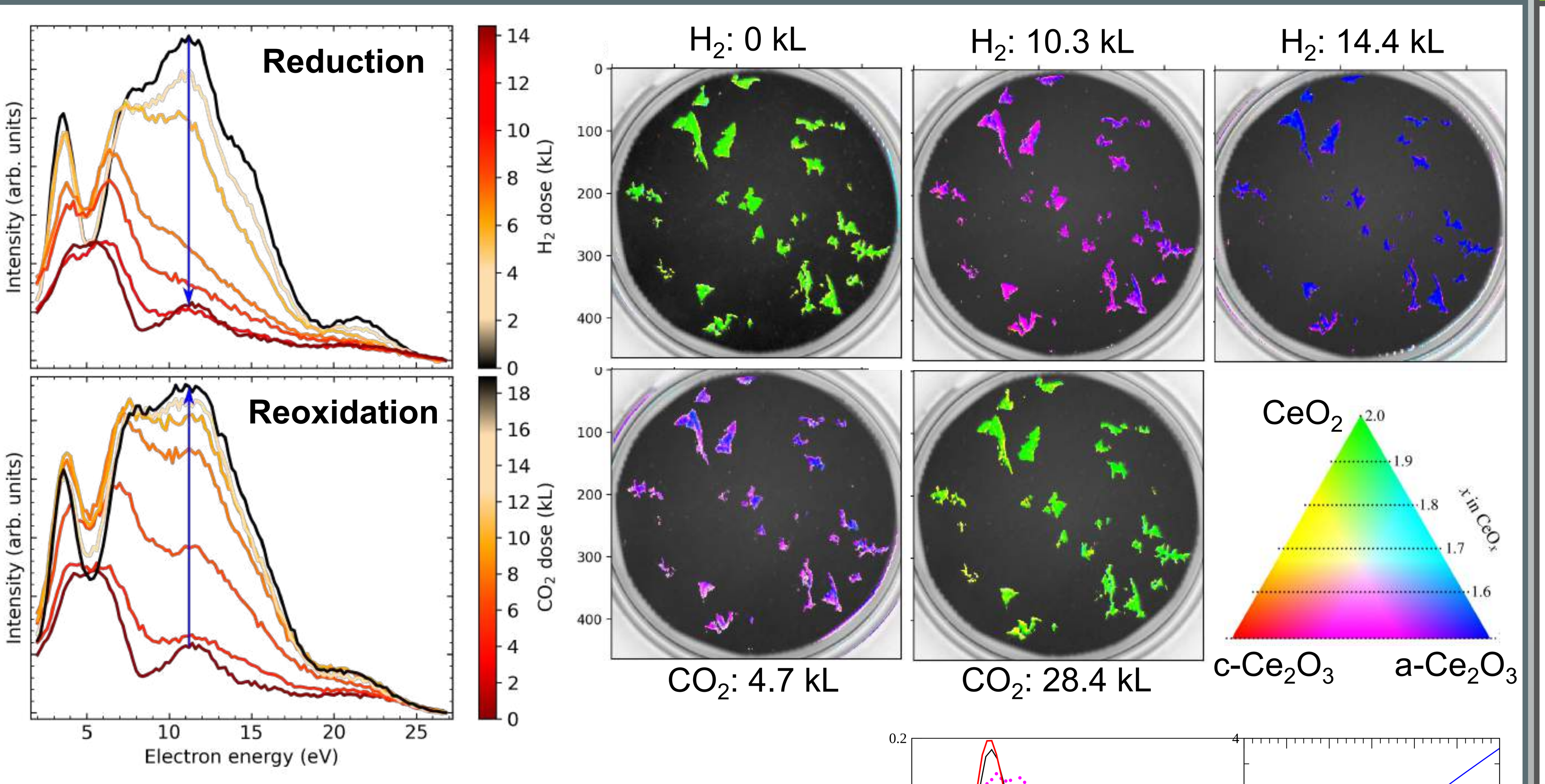
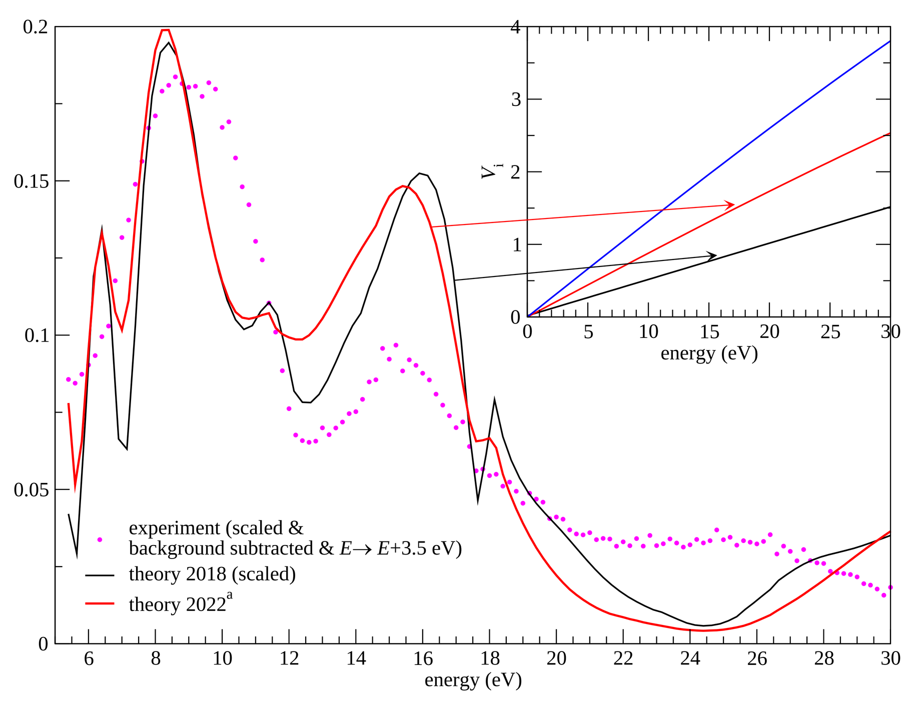


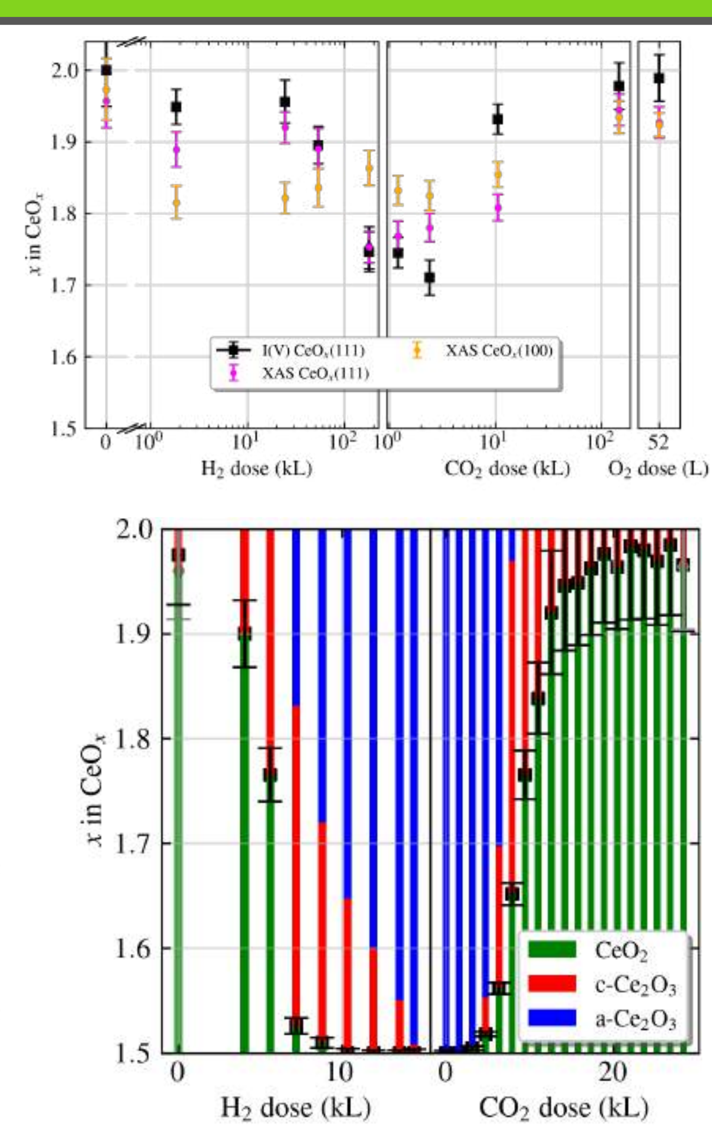
Figure 4. Dynamic I(V)-LEEM Reduction (left top), reoxidation (left bottom) and pixel-wise decomposition analysis [7-9] of the I(V) stacks in single images with increasing H_2 dose (0, 10.3 kL, 14.4 kL) and CO_2 dose (4.7 kL, 28.4 kL) (right). The triangle details the color map denoting the cerium cation oxidation state in the false-color images (right).

(bottom right) First identification of hexagonal Ce_2O_3(0001) by comparison with ab initio scattering calculations [7, 10].



Summary and conclusions

- Reduction and reoxidation in agreement with literature [3,6]; stronger reduction achieved with higher H_2 dose.
- CeO_x(100) I(V) curve becomes featureless upon reduction and is not recoverable during reoxidation ⟹ loss of surface crystallinity
- Further redox cycles only need lower H_2 and CO_2 doses.
- CeO_2(111) reduces from the defects within the islands and reoxidizes starting from the island edges.



References and Acknowledgments

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