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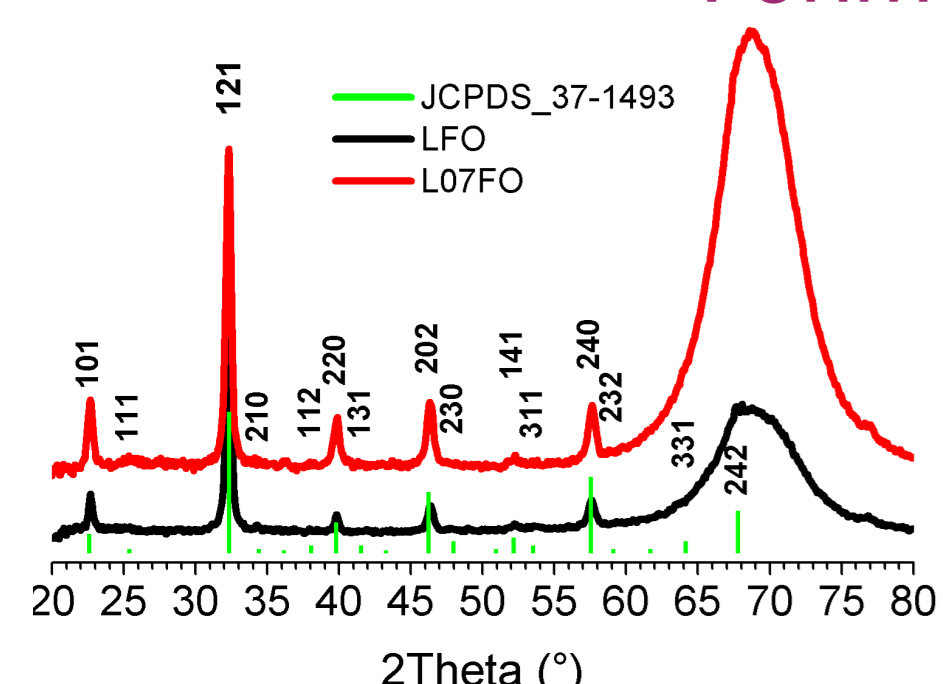
On the tracks of surface dynamics of LaFeO₃-based perovskites

Abstract. LaFeO₃-based mixed oxides of mostly ABO₃ perovskite structure are promising materials for key surface redox processes, such as three-way catalysis (TWC) or oxygen reduction at solid oxide fuel cell (SOFC) cathode. By taking advantage of the versatility of the perovskite structure, it is possible to prepare modified oxides with drastically increased performances as compared to the parent LaFeO₃. Here, we explore the effect of La deficiency on the dynamics of selvedge under model redox excitation. We show here the results of a unique combination of sample- and technique-based strategies to explore the surface / subsurface dynamics of La_{0.7}FeO₃ at the right place, in proper time and under redox-relevant conditions.

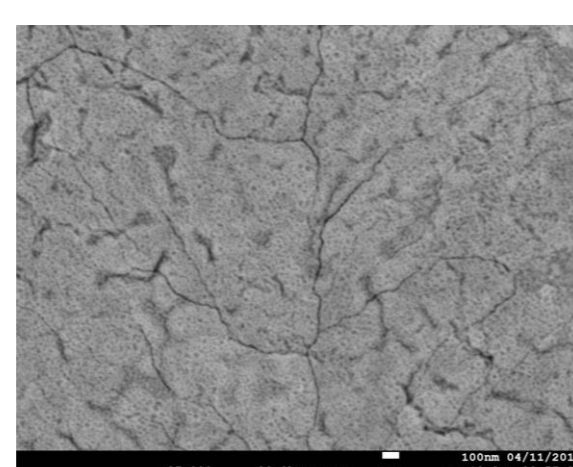
WHY (and HOW) is La_{0.7}FeO₃ (moderately) active in TWC while stoichiometric LaFeO₃ is absolutely non-active? ?

From sample design

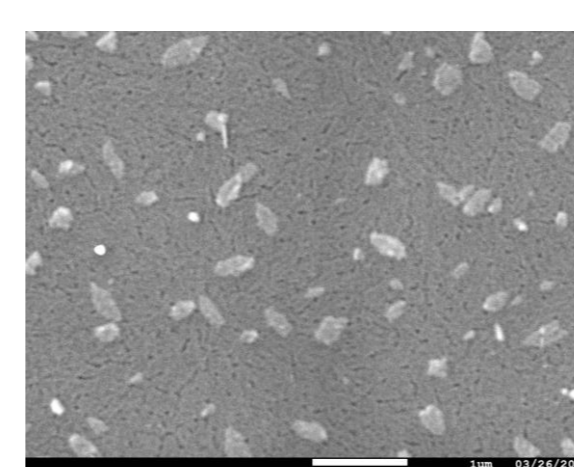
Model oxide thin films of LaFeO₃ vs. La_{0.7}FeO₃
citrate-complex sol spin-coated over passivated Si (100)
~ 70nm thick, calcined at 650° C



LFO



L07FO

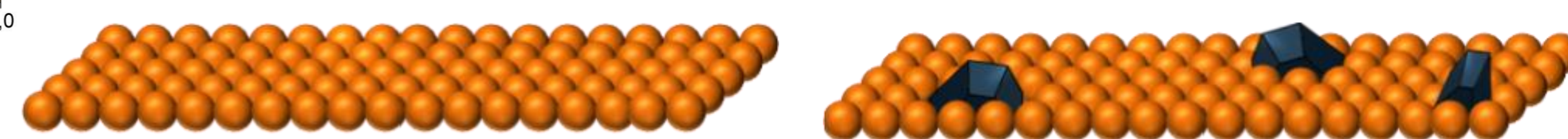


- Representative of powder-shaped LFO surrogate
- Allows surface-relevant investigation
- Higher selvedge representation

Short-range structure (Raman, XAS): presence of α-Fe₂O₃ nanophase as islands over LFO

LFO

L07FO



Same long-range crystal structure (perovskite)...

... BUT distinct textural properties

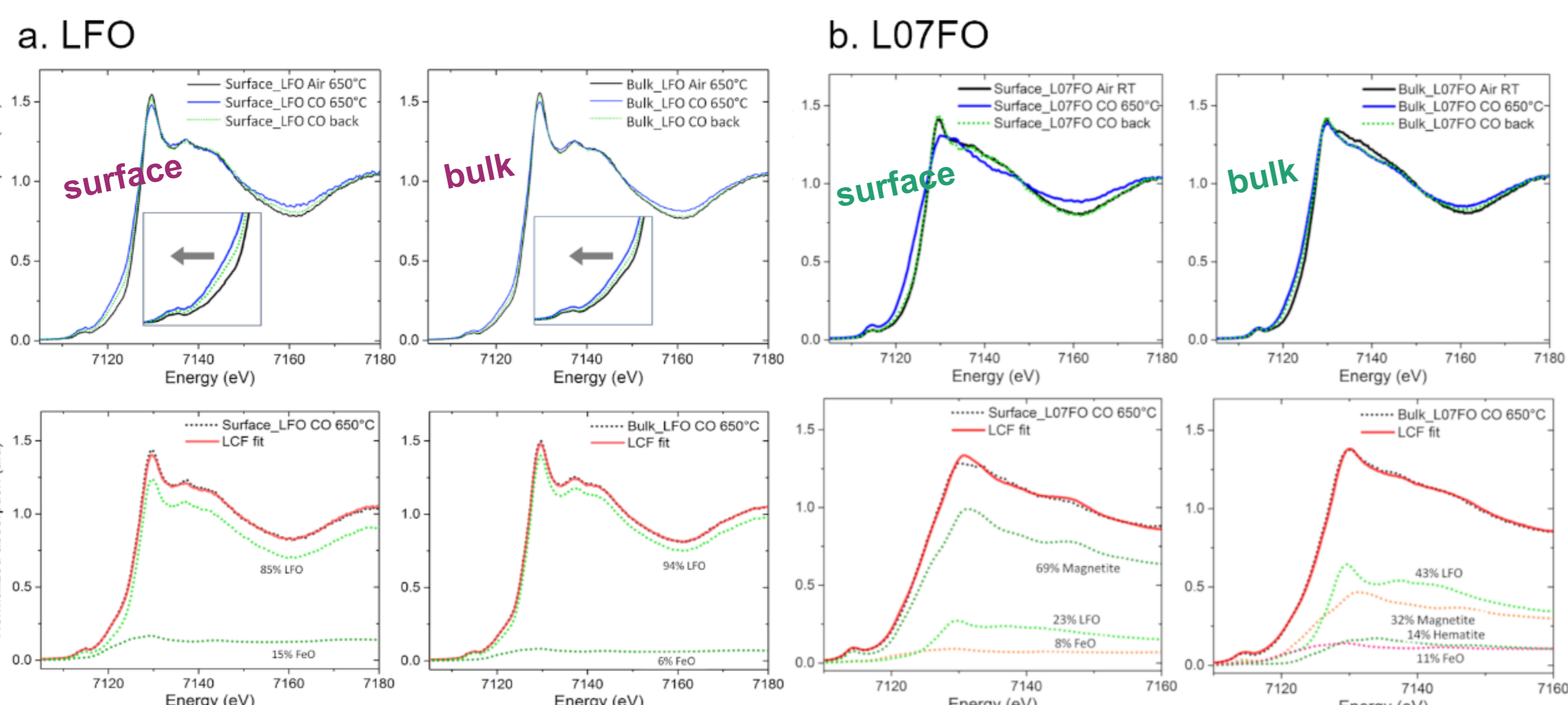
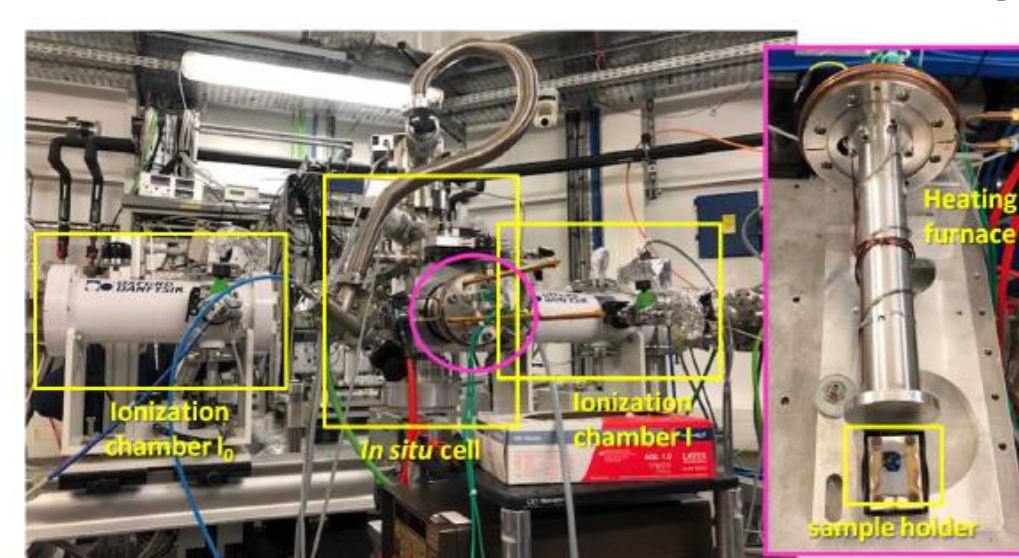
to surface-relevant *in situ* investigations under CO/O₂ cycling:

Follow-up of short range organisation of Fe species and of the oxidation state of Fe and La

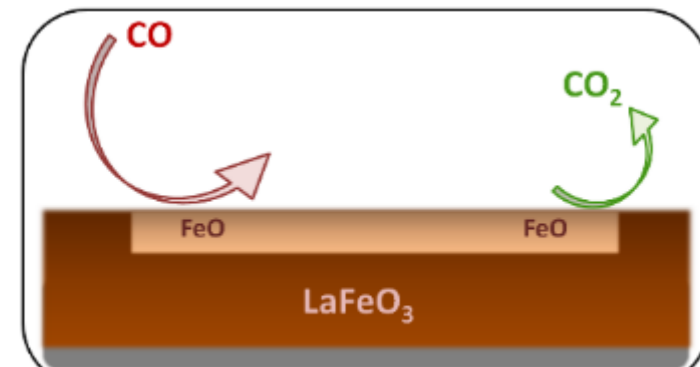
Grazing incidence X-Rays absorption spectroscopy (GI-XAS)



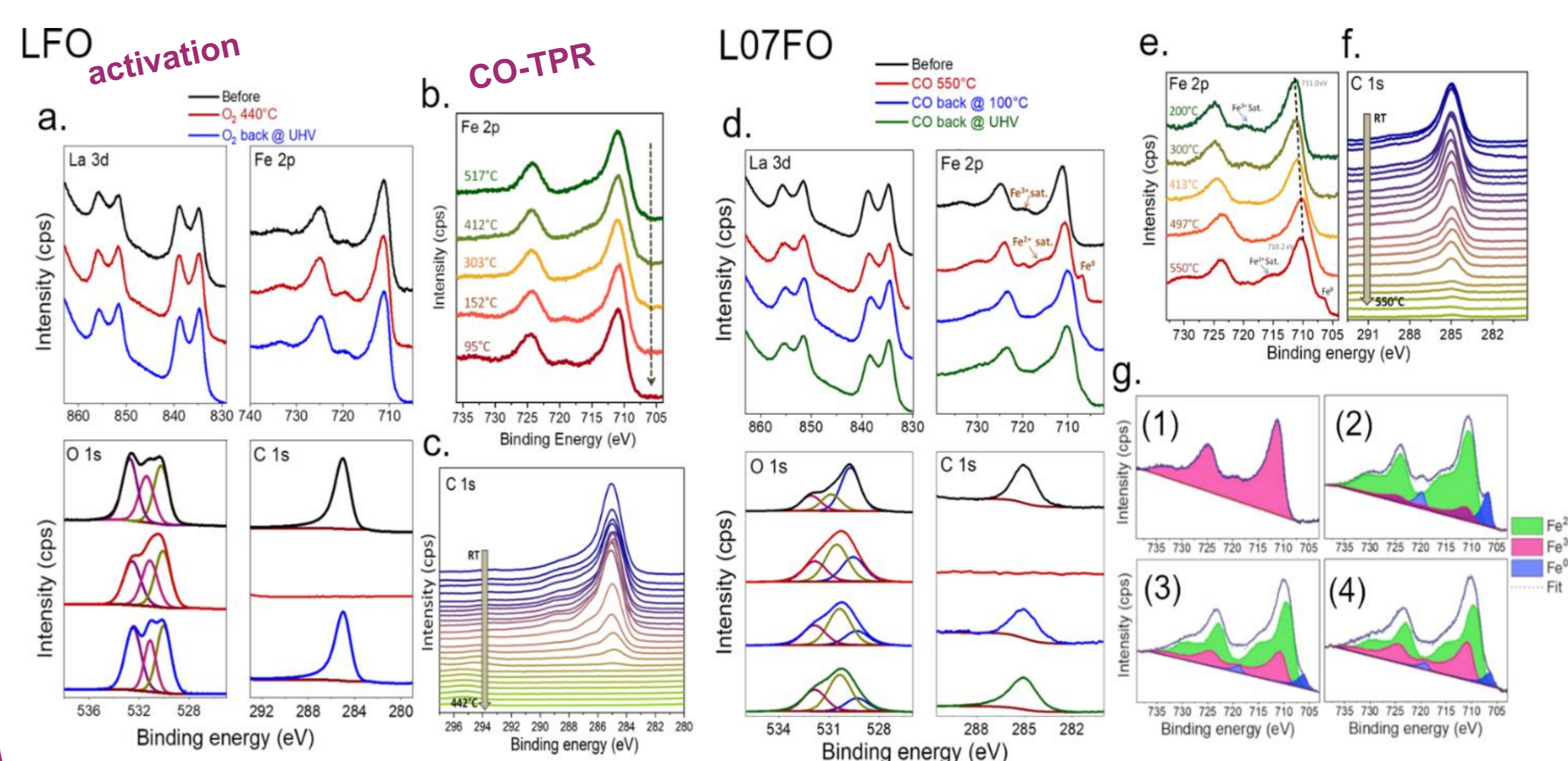
Near-ambient pressure XPS (NAP-XPS)



Limited reduction of LFO to Fe^(II)O on surface

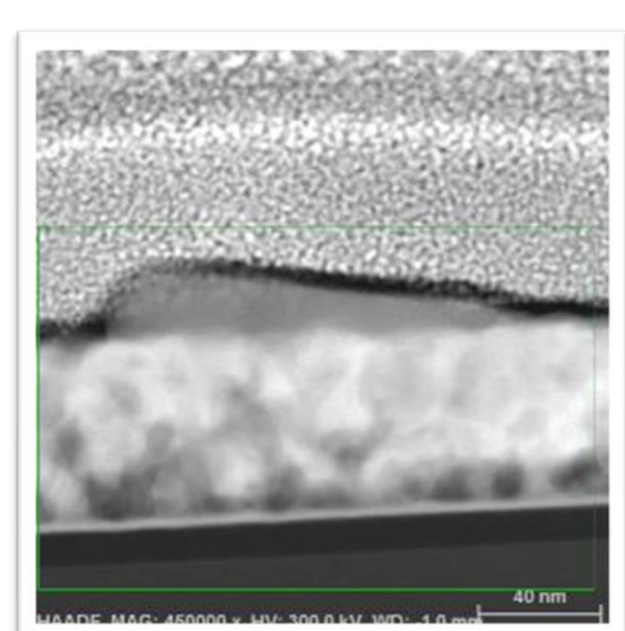


Substantial reduction of Fe^(III)2O₃ to Fe₃O₄ (II, III) on surface; limited reduction of LFO to FeO



Under CO: minority reduction of Fe from +III to +II o.s. for LFO significant reduction from +III to +II and even 0 o.s. for L07FO La fully remains in the +III state

What have we learnt?



- The Fe₂O₃ phase is exsolved from the LFO forming flat islands with large contact surface
- Fe₂O₃ islands and the LFO get both reduced / re-oxidised upon redox cycling
- At the interface between the iron oxide and LFO phase stands the secret for closing of the cycle thanks to the formation of Fe₃O₄
- LaFeO₃ is acting like a reservoir of FeO

