Establishing Structure-Sensitivity of Ceria Reducibility: Real Time Observations of Surface-Hydrogen Interactions

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Details of the preparation process: Figure S1 shows LEEM images of the preparation process. The clean Cu (111) single-crystal was annealed at 870 K in an atmosphere of 5×10^{-7} mbar of oxygen partial pressure right before cerium deposition, which helped to further decrease the amount of carbon impurities on the surface and to establish a well-defined surface oxygen chemical potential. No visible defects or imperfections are present in the observed region of the substrate, although other parts of the single-crystal might be affected by such structures.¹ The mean terrace width of the prepared substrate is of the order of tens to hundreds of nm (Figure S1(a)), indicating very flat and well-defined growth support.

The ceria growth is done by evaporation of cerium metal in the same oxygen ambience. Immediately after the beginning of the cerium deposition, the nucleation of ceria islands starts, and several structures are formed within the observed field of view (Figure S1(b)), with their nucleation sites pinned to the substrate's step boundaries. As the growth process continues, the step boundaries bend to accommodate the presence of the growing ceria islands (Figure S1(c)).



Figure S1. LEEM images (recorded at 1 eV) during growth of ceria islands on Cu (111) substrate in 5×10^{-7} mbar O₂ at 720 K: (a) clean substrate, (b) after 30 s, (c) after 10 min of growth.

The different surface orientations of islands can be distinguished by intensity-voltage LEEM.² Depending on the electron beam energy with respect to the sample potential (also called start energy), the two surface orientations show different intensities as a result of their different low-energy electron reflectivities.³ Using a LEEM start energy of 9 eV in Figure 1(b), the (111) islands appear brighter than the (100) ones. The ultimate confirmation, however, comes from the μ -LEED measurements.

Determination of CeO_x island thickness: Figure S2 shows Cu L3 XAS spectra extracted from the exposed substrate and from below the grown islands that were used for the islands' thickness determination.



Figure S2. Cu L_3 edge X-ray absorption spectra extracted at three different locations on the sample: (a) with subtracted pre-edge; (b) normalized to the same step-edge difference showing the overlap of the spectral shapes, which rules out the difference in Cu chemical state on the surface and under the islands.

Stoichiometry in X-PEEM: The difference in ceria reduction can be seen in the X-PEEM images of the islands taken at the photon energy corresponding to the Ce^{4+} peak (883.4 eV). In Figure S3 (a) the islands are shown in their uniform oxidation state after the growth and in Figure S3 (b) they are shown after 18 h in hydrogen. The sole (111) island in Figure S3 (b) is visibly brighter than all the other islands, which reveals its higher Ce^{4+} content.



Figure S3. X-PEEM images at Ce M₅ edge (hv=883.4 eV) of the CeO₂ (111) and (100) islands in Figure 2(a): (a) after growth, measured in 5×10^{-7} mbar O₂ at 700K; (b) after 18 h in 1.5×10^{-6} mbar H₂ at 700K.

Details on theoretical calculations: Initial theoretical calculations were based on density functional theory (DFT) in the implementation with plane waves and pseudopotentials using the generalized gradient corrections to the local density functional approximations as proposed by Perdew et al. (PBE).⁴ In addition, we employ a Hubbard correction (+U) according to the method proposed by Dudarev et al. to accurately treat the strongly correlated f -electrons in Ce.⁵ Our simulations include non-spherical contributions from the gradient corrections inside the PAW spheres using the flag LASPH = .TRUE. in the VASP input. All calculations have been made with a U-value of 5 eV which has been shown to give a good description of stoichiometric and reduced ceria in previous studies.^{6,7,8,9} Results in table S1 show oxygen vacancy

formation	energies	as a	function	of the	different	level	of ceri	a reduction	for	the	two	respective	surface
terminatio	ons of 3M	L thi	ck slabs.										

(111)		(100)	
E _{vac} [eV]	$C(Ce^{4+})$	E _{vac} [eV]	$C(Ce^{4+})$
1.330	0.958	0.650	0.917
1.540	0.833		
2.060	0.667	1.380	0.667
2.230	0.333	2.230	0.333

Table S1. Calculated oxygen vacancy formation energies E_{vac} for different ceria stoichiometry (shown as Ce⁴⁺ concentrations) and surface termination using DFT+U.

Another approach in theoretical simulations was based on DFT in the implementation with plane waves and pseudopotentials using the Hybrid density functional proposed by Heyd-Scuseria-Ernzerhof (HSE06).^{10,11} Table S2 shows the calculated oxygen vacancy formation energies for the different Ce⁴⁺ concentrations in a three ML slabs of ceria (111) and (100).

(111)		(100)	
E _{vac} [eV]	$C(Ce^{4+})$	E _{vac} [eV]	$C(Ce^{4+})$
2.382	0.958		
2.383	0.917	1.611	0.917
2.771	0.833		
3.332	0.667	2.538	0.667
3.419	0.333	3.175	0.333

Table S2. Calculated oxygen vacancy formation energies E_{vac} for different ceria stoichiometry (shown as Ce^{4+} concentrations) and surface termination using hybrid density functionals.

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