Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information to: Thermal reduction of ceria nanostructures on rhodium(111) and re-oxidation by CO_2

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This file contains additional, original data supporting the main article. Description of the figures can be found in their respective captions.

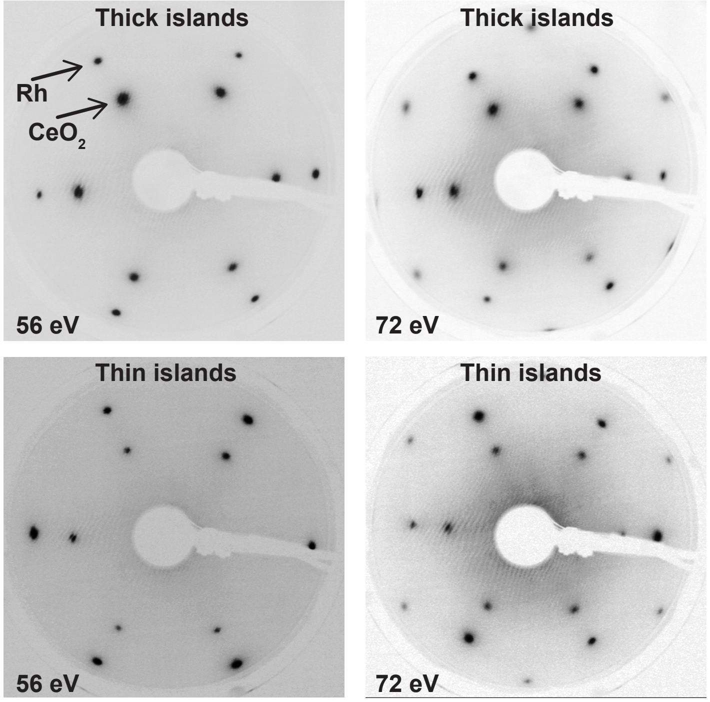

Figure S 1 *LEED images of the surfaces containing the thick (top) and thin (bottom) islands measured at two different electron energies. The LEED images show that the oxide grows in (111) orientation in registry with the Rh(111) substrate. The CeO_2 -spots appear slightly more intense for the sample containing the thicker, larger islands. However, overall the intensities are very similar despite the different coverages, indicating a comparable amount of uncovered Rh surface area, as it is also hinted by the Rh 3d signals in PES. The ratio Rh/CeO_2 of the lattice parameters is 1.4, as reported in previous studies.*

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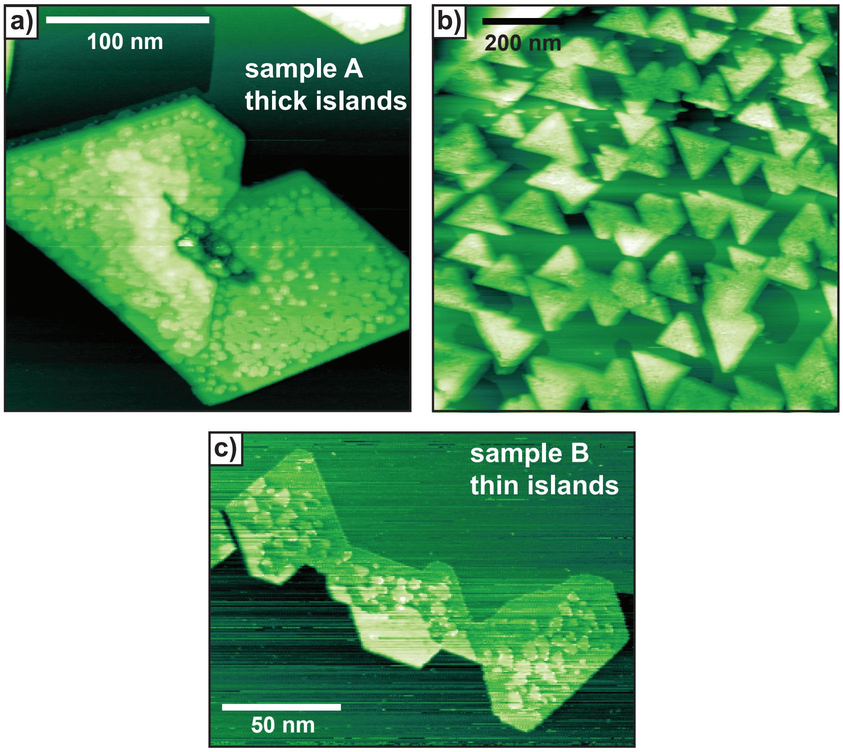

Figure S 2 *STM images obtained after preparation of the ceria islands on Rh(111). a) and b) sample A, thick islands. a) shows two islands each more than 100 nm in diameter that started to nucleate from a central defect or impurity, forming a boundary region. Like the island described in the main text the islands consist of three closed trilayers as a base while the following layers are open and formed by small islands. b) large scale image (1x1 µm*) c) a cluster of thin islands decorating a step edge of the substrate. The bright area in the center shows a second trilayer forming while other areas still contain many small nucleates of the second layer.

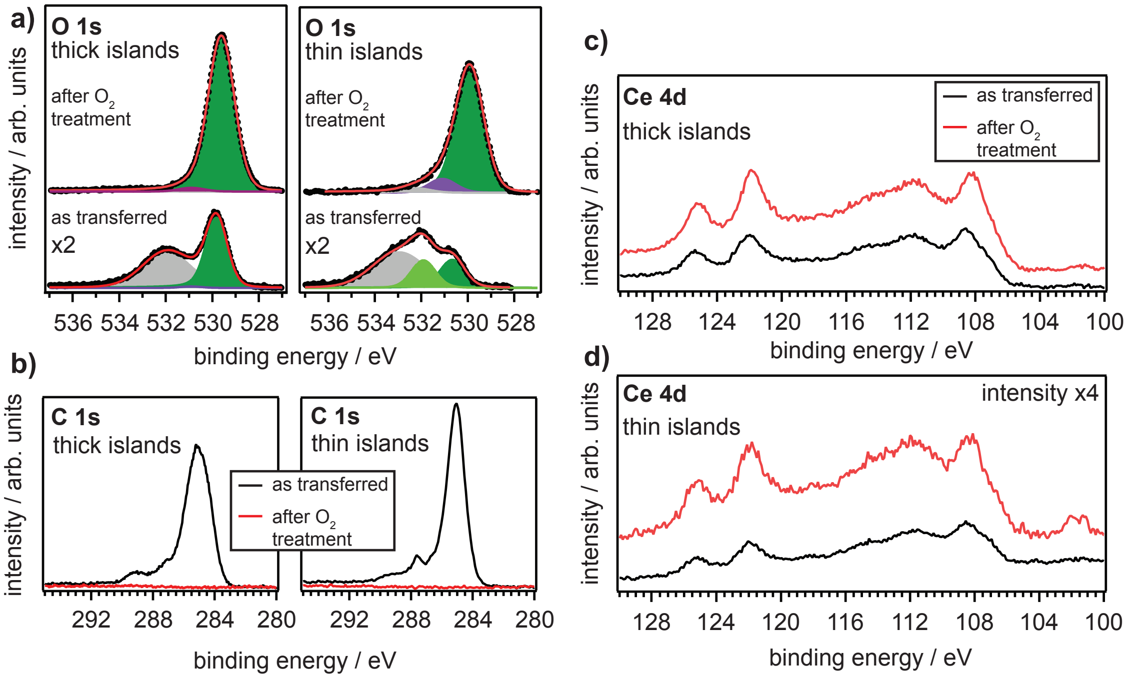

Figure S 3 *Spectra of the as-transferred samples and after cleaning at elevated temperature in 1.3x10^{-5} hPa oxygen. a) O 1s spectra: the as transferred spectra (bottom) contain several components. The component at highest binding energy (grey) is likely stemming from OH groups. The thin islands appear to be covered by more material, as the oxide signal (dark grey) is attenuated stronger. The oxygen treatment removes the contaminants effectively. b) C 1s spectra: The sample containing thin islands exhibit a more intense carbon signal. Both spectra contain a small amount of intensity at higher binding energies, probably originating from carboxylates and other CH_yO_x species collected during exposure to the air. c) & d) Ce 4d spectra before and after (red) the cleaning procedure. In both cases the signal becomes more intense. The relative intensity of the doublet between 121-126 eV also increases reflecting a higher Ce^{4+} content after the oxygen treatment. If plotted properly normalized both spectra appear virtually identical within the accuracy of the measurement, as shown in the main document.*

Determination of the oxidation state of the ceria islands

The stoichiometry of the ceria deposits was determined by linear combination of the most oxidized and most reduced Ce 4*d* spectrum obtained. In the following we describe the methodology employed and assumptions that were made for the evaluation.

We start with the assumption, that the most oxidized spectra correspond to CeO_2. Because the reduced spectrum of the thin islands appears slightly more reduced we will employ that spectrum for the further analysis. It will set the maximum reduction we can possibly detect. The procedure used to describe each spectrum of the reduction series is then as follows: Following equation 1 we always start with $\omega = 1$, i.e. 100% of the oxidized spectrum. The weight of the CeO_2 spectrum is then reduced in steps of 10^{-4} while the weight of the reduced spectrum increases correspondingly.

$$\omega \cdot CeO_2 + (1-\omega) \cdot Ce_2O_3 \approx CeO_x \tag{1}$$

The result of the linear combination is then subtracted from the spectrum to be fitted. The procedure continues until an minimum for the area of the squared difference spectrum is reached. Following the described procedure fig. 3 (main text) is obtained. The left ordinate in fig. 3 (main text) corresponds to the weight of the CeO_2 spectrum in the linear combination. For the thin islands ω nearly reduces to zero. Averaged over the last 5 data points, a residual weight of $\omega = 0.04$ is remaining at the most reduced situation. This means, that either 4% of Ce^{4+} is remaining or that the most reduced spectrum used in the linear combination contains 4% of Ce^{4+}. In both cases a stoichiometry of $CeO_{1.52}$ ($Ce^{4+}_{0.04}Ce^{3+}_{0.96}O_{1.52}$) results for the most reduced spectrum. An additional source of error in this evaluation is the assumption, that the most oxidized spectrum corresponds to CeO_2. Because both, thick and thin islands exhibit a virtually identical Ce 4*d* spectrum after the oxygen treatment we do not expect a large error caused by the above mentioned assumption. Taking into account, that the reduced spectrum used for the linear combination may still contain up to 4% of Ce^{4+}, as an upper

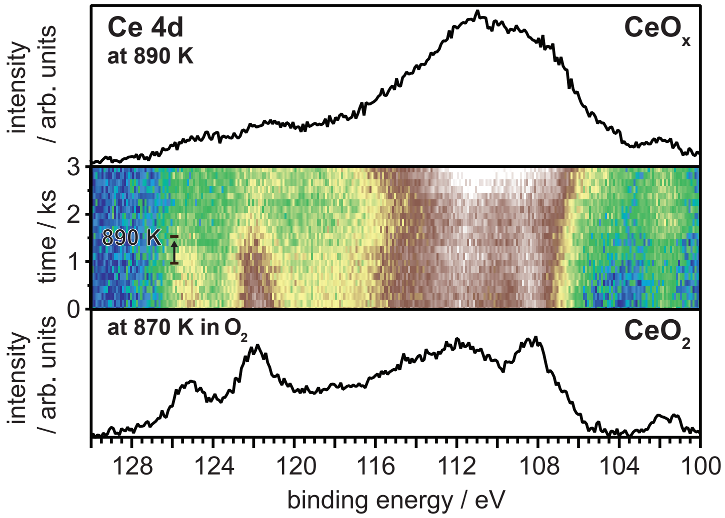

Figure S 4 *Evolution of Ce 4d spectra of the thin islands (sample B) during thermal reduction. The bottom spectrum is measured in 1.3x10*$^{-5}$ *hPa oxygen. The oxygen is pumped out and the continuous measurement (middle section) started. At the point indicated the temperature was increased to 890 K and kept until the end of the measurement. The upper spectrum was measured at 890 K in vacuum.*

bound, a stoichiometry, i.e. the x in CeO$_x$, can be obtained following:

$$x = 0.5 \cdot (\omega + \beta) + 1.5 \tag{2}$$

$$\beta = (1 - \omega) \cdot 0.04 \tag{3}$$

with β being the additional weight delivered by the residual Ce^{4+} in the reduced spectrum. The stoichiometric number x is displayed as the right ordinate in fig. 3 in the main text. Figure S5 e) presents an example for an intermediate spectrum of a reduction series described by the two reference spectra.

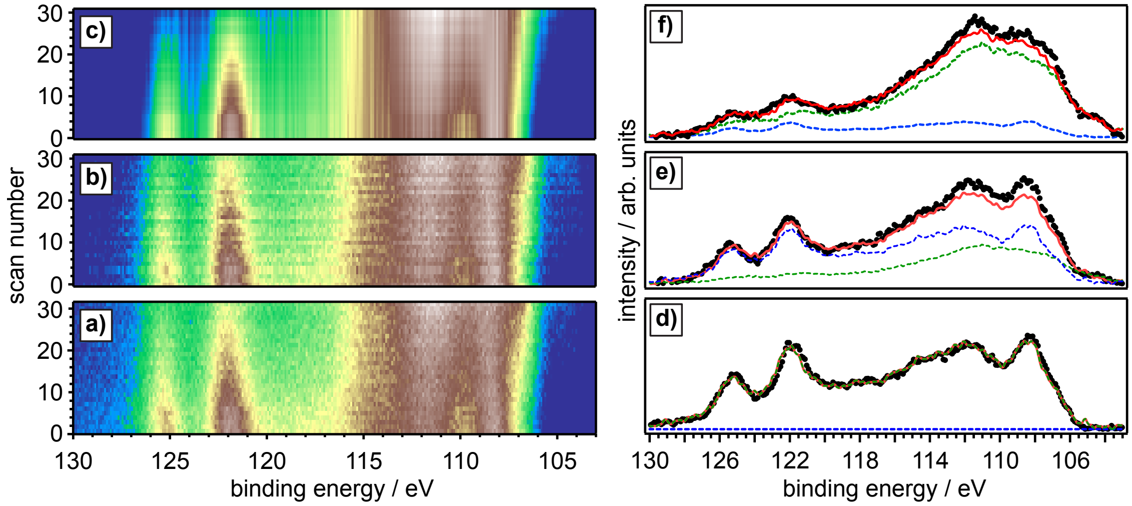

Figure S 5 *Results of the linear combination procedure employed to fit the Ce 4d spectra. a) as measured spectra during thermal reduction of the thick films b) after background subtraction c) result of fitting every slice with a linear combination of the most reduced and most oxidized spectrum of the thin islands. The main features are reproduced well. d) Most oxidized spectrum of the thick islands prior to reduction. Virtually identical with the spectrum of the thin islands e) intermediate spectrum. Ce*$^{4+}$ *features described well. f) most reduced spectrum of the thick films. Still needs a small amount of the most oxidized spectrum for good description. The lower intensity in the region around 110 eV is likely a result of the background subtraction.*

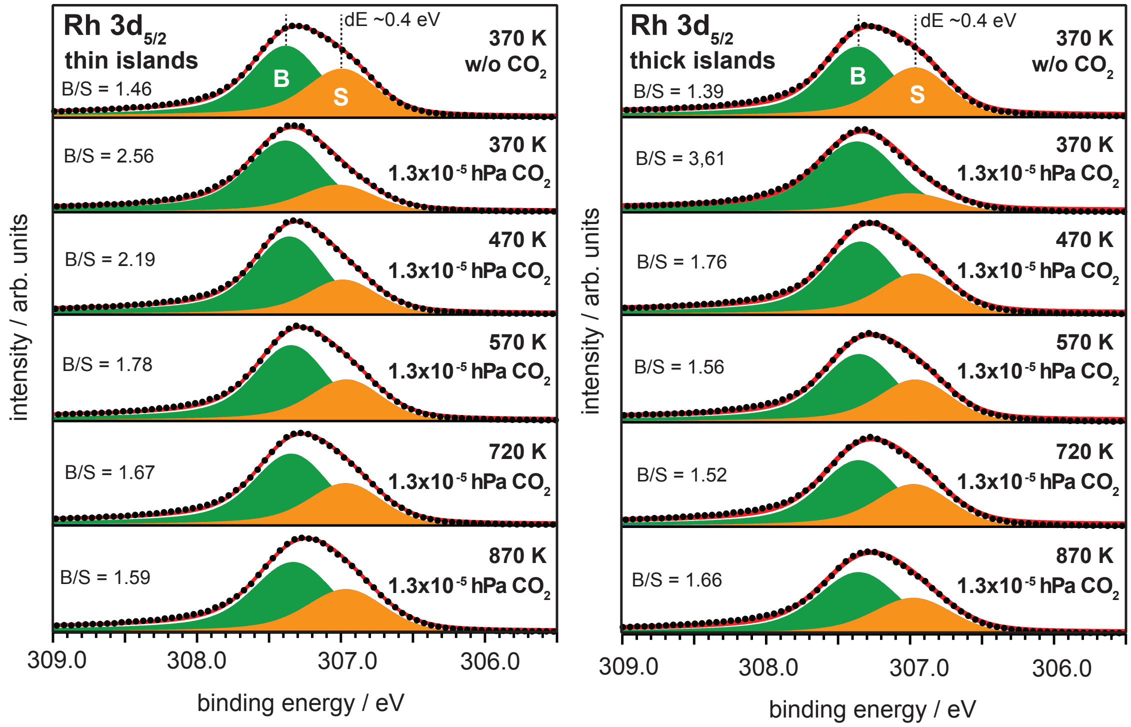

Figure S 6 *Evolution of Rh 3d$_{5/2}$ spectra in the static experiment (see main text) before (top spectra) and during heating the reduced samples in CO$_2$ at the sample temperature indicated in the figure. The bulk and surface components are denoted B and S, respectively.*

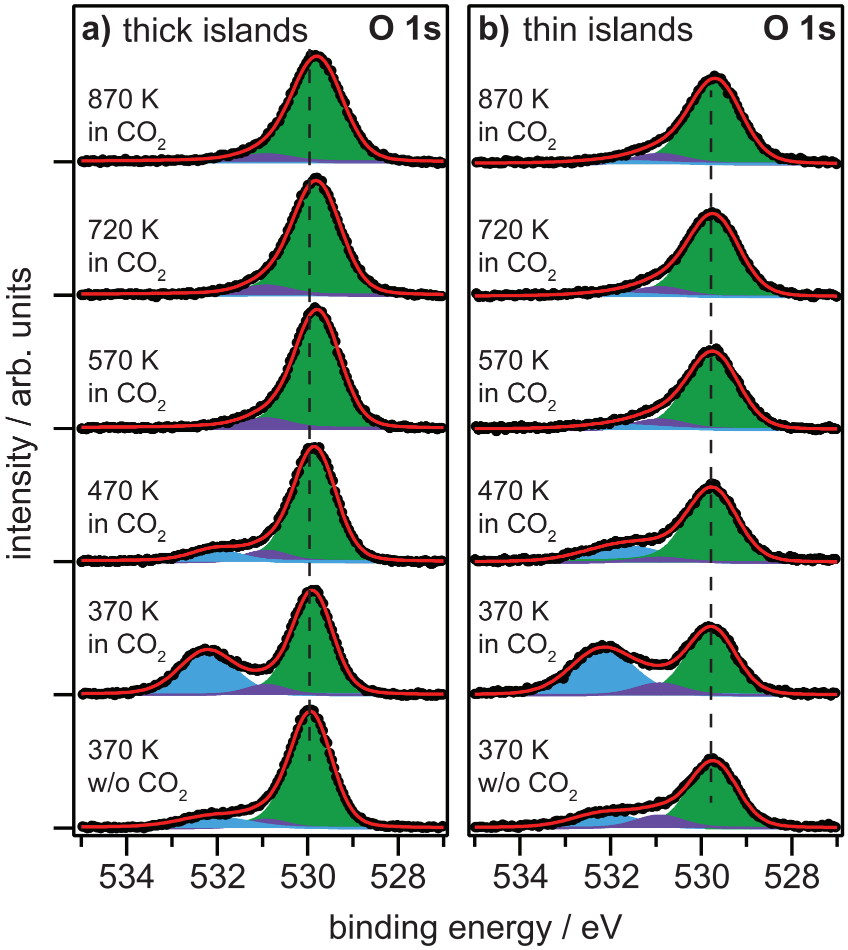

Figure S 7 *Complete set of the O 1s spectra obtained in the static experiment (see main text) before (bottom) and during heating the reduced samples in* CO_2 *at the sample temperature indicated in the figure.*