Size Control of Pt Clusters on CeO$_2$ Nanoparticles via an Incorporation-Segregation Mechanism and Study of Segregation Kinetics

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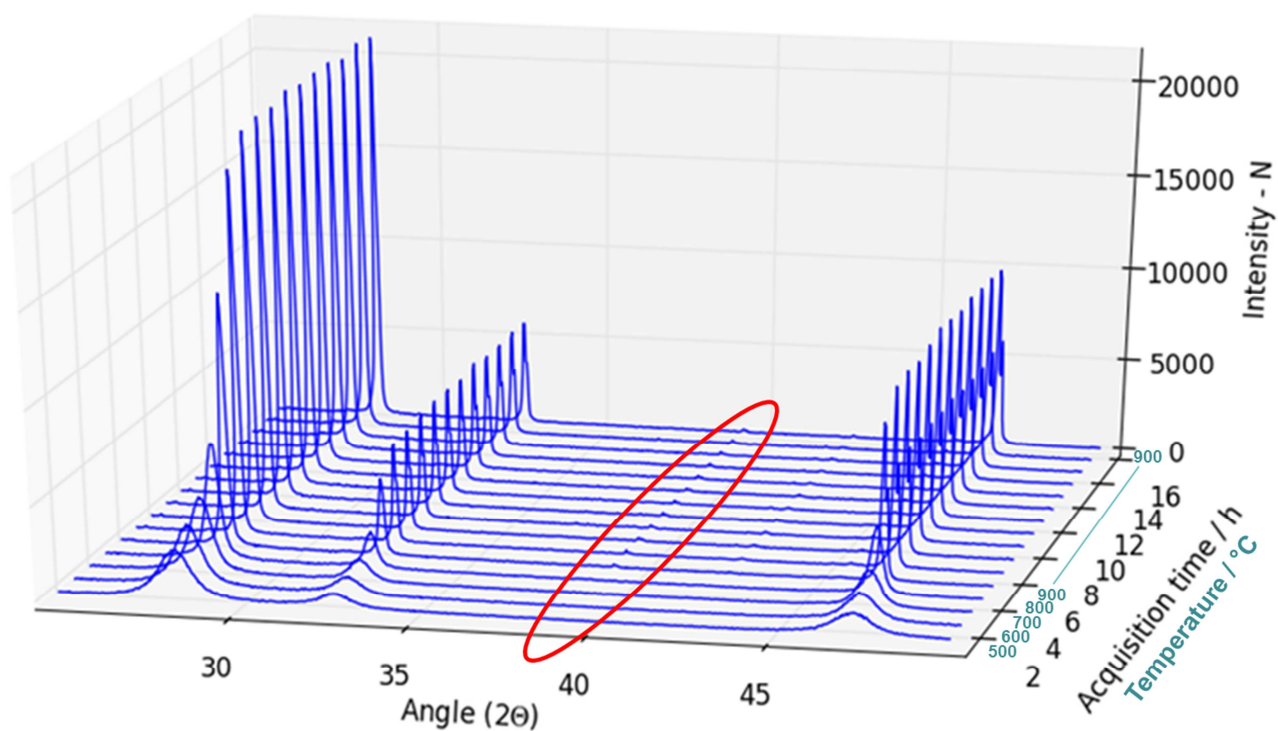
Contents:

Figure S1. *In-situ* XRD measurements to screen the CeO_2 and Pt peak evolution up to 900 °C. XRD patterns of a thermally pretreated sample with high Pt load (7wt%, 500 °C/3 h, H2) were acquired for increasing temperatures (500-900 °C, 1 step = 100 °C) during 1 h acquisition time per temperature. The Pt peak becomes XRD-visible only after 1 h at 900 °C (marked area). Further patterns were recorded over 12 h (1 pattern / h) at 900 °C.
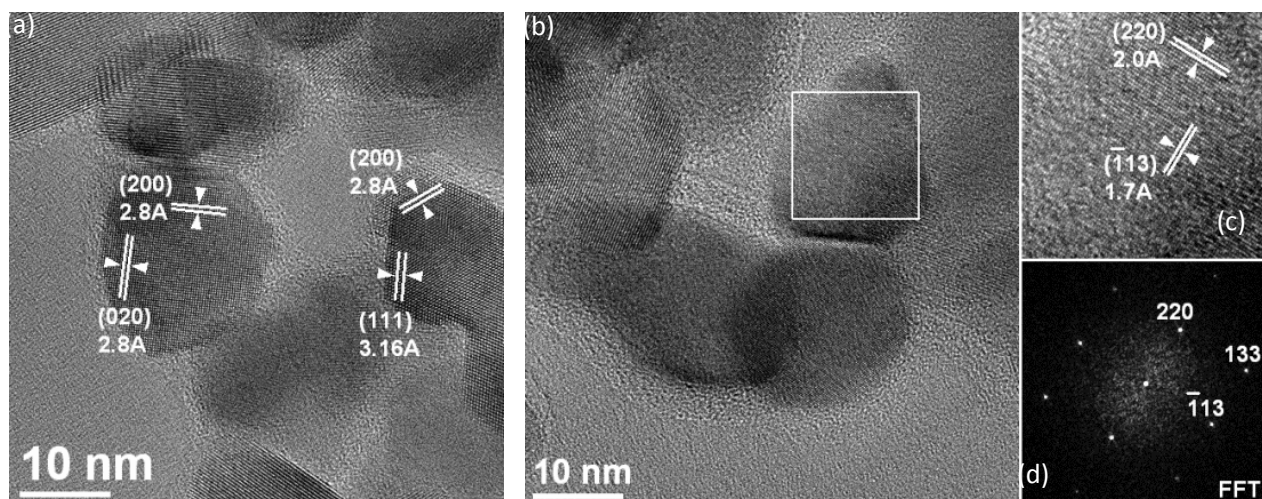
Figure S2. HR-TEM micrographs of sample H6 (900 °C, 0.5 h). In (a) the lattice plane of CeO$_2$ crystals are shown. In (c) is reported the high magnification of the zone indicated in (b); in (d) the corresponding Fast Fourier Transformed image of (c) is shown. No evidence of Pt segregation could be detected.
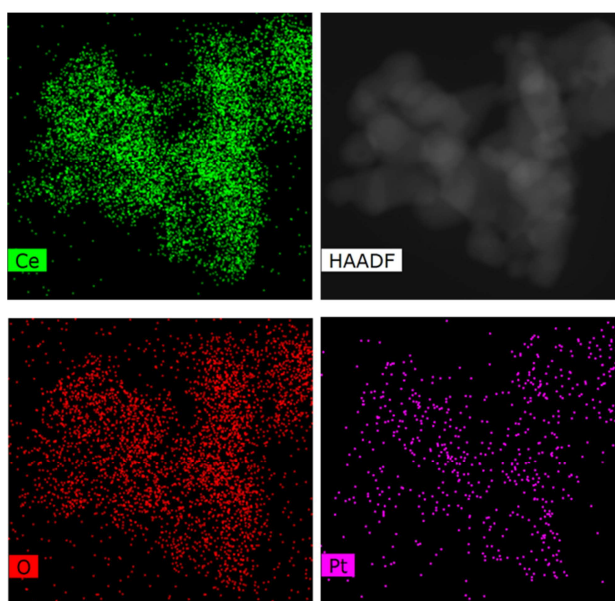
Figure S3. EDX chemical mapping of sample H6 (900 °C, 0.5 h). The HAADF image (top right) is shown together with the elemental mapping of cerium (top left), oxygen (bottom left), and Pt (bottom right). There is no apparent zone with distinct higher Pt content. Moreover, the signals are equally distributed over the sample. This is a further proof, that the Pt is ionically dispersed under these treatment conditions rather than clustered in form of metallic islands on the surface.
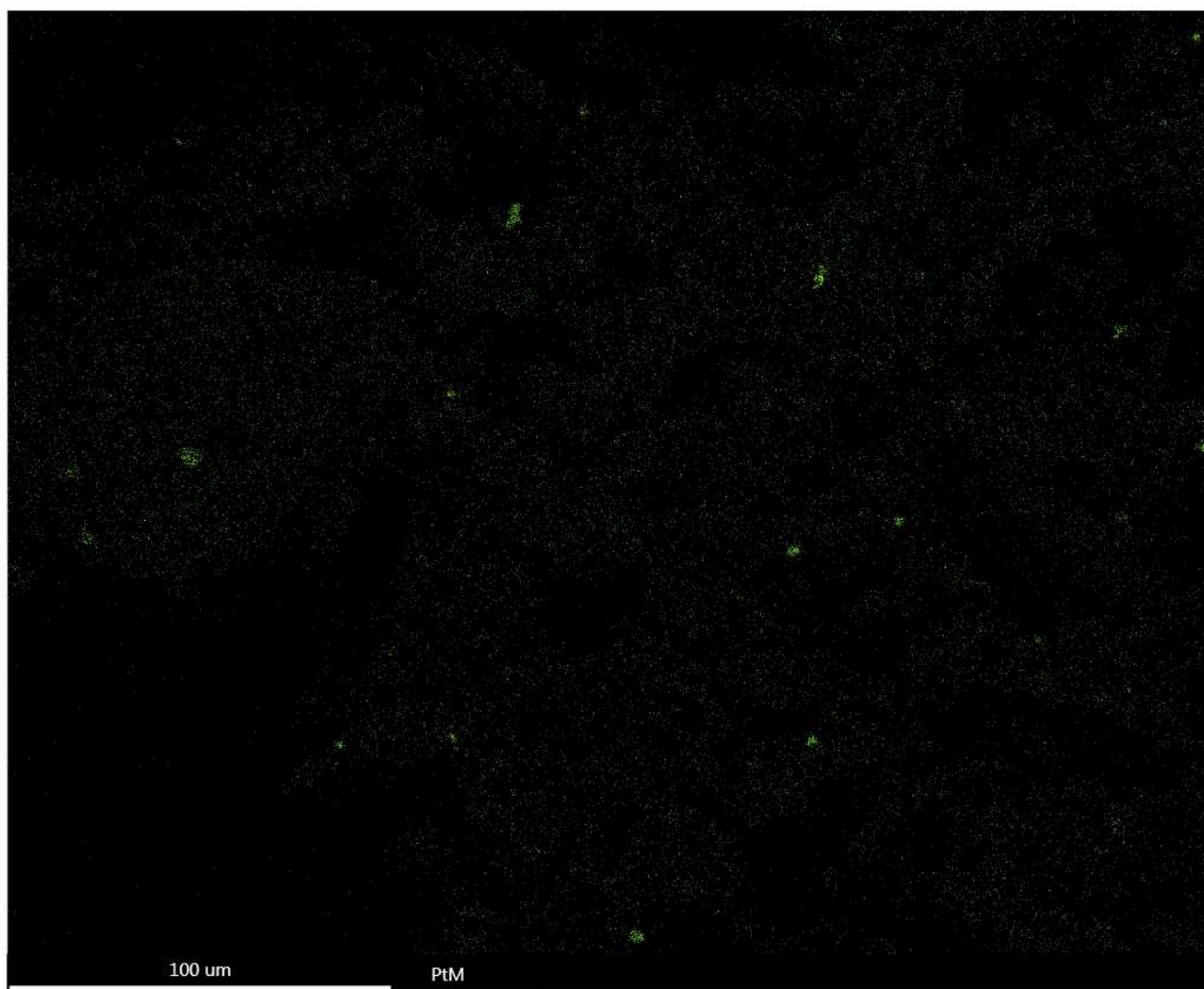
Figure S4. EDX chemical mapping of sample L_ox7. The green spots correspond to higher concentrations of Pt, which could be identified as micrometer-sized Pt particles in the FE-SEM images. There is one particle in about 5000 μm^2 of scanned surface sample.
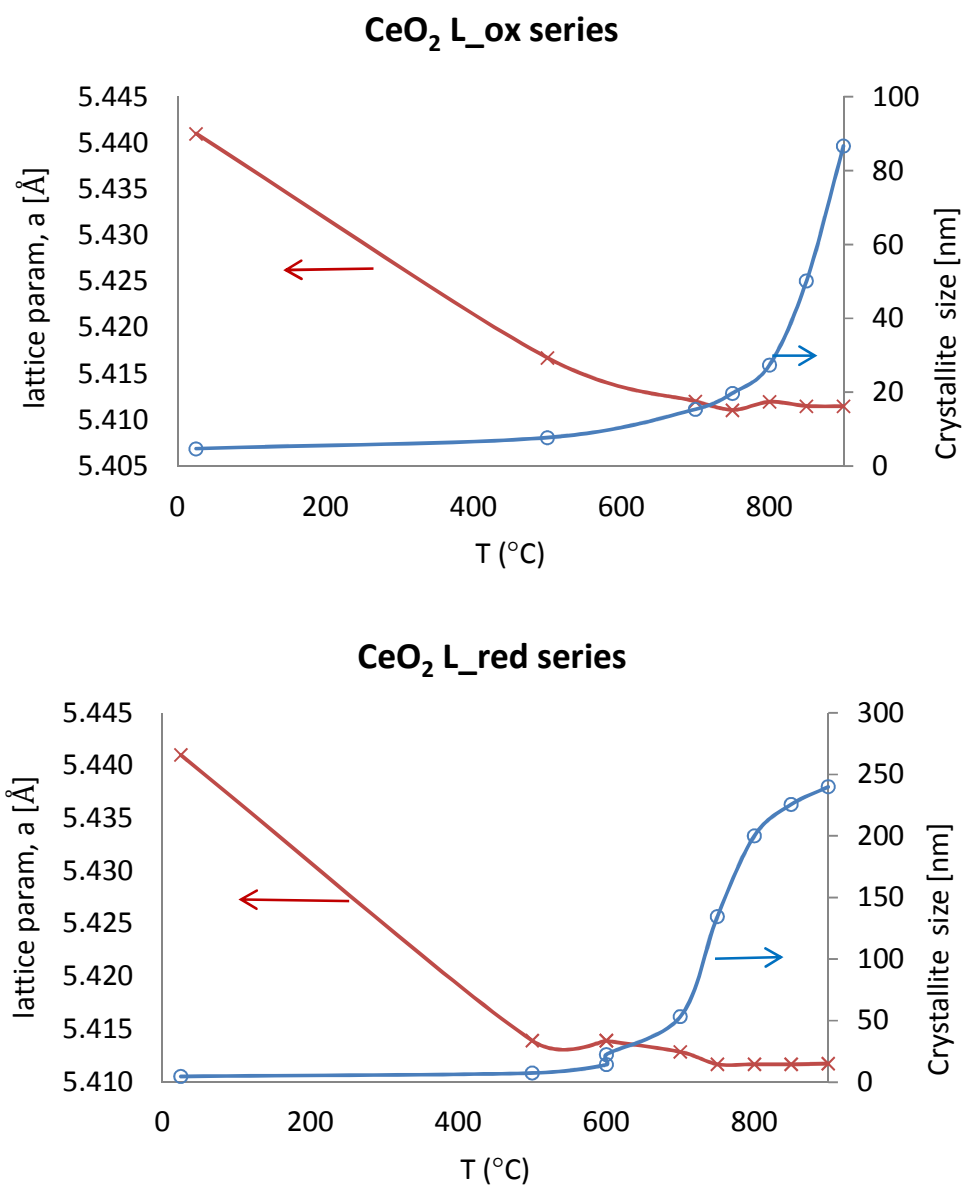
Figure S5. CeO$_2$ lattice parameter (*a*) and crystallite size calculated by Rietveld refinement using the full pattern.

Table S1. Treatment temperatures for the respective samples of the K series and the calculated kinetic constants for the Pt segregation. The values are derived from the slopes of the normalized integrated intensities of the Pt (111) peak ($\overline{I_{Pt(111)}}$) over time.

Sample	Treatment temperature $T\,/\,°C$	Kinetic constant k / dimensionless
K1	930	5.417E-06
K2	940	9.544E-06
K3	950	3.073E-05
K4	960	3.921E-05

Comments Particle statistics effect:

Considering that the capillary is rotating on its axis, that is normal to the diffraction plane, only and all crystallites whose Bragg planes for a given (*hkl*) reflections are close to orthogonal to the diffraction plane will contribute to the (*hkl*) Bragg peak, as in some moment during the rotation they will be in perfect diffraction condition.

The condition to be "close to orthogonal to the diffraction plane" can be better practically specified as to have an orientation such that the diffracted beam hits the detector. The latter has an opening of 8 mm orthogonal to the diffraction plane and the distance is 762.5 mm from the sample; therefore, the allowed angular deviation from the diffraction plane is $\pm$ (1/2)*(8/762.5) in radians, that makes $\pm$ 5.2 mrad. The total acceptance is then 10.4 mrad - or 0.6 deg.

The lattice planes can be rotated anywhere from 0 to 180 deg with respect to the diffraction plane, with uniform probability; therefore the fraction of "captured" grains is $0.6/180 = 3.3 \cdot 10^{-3}$.

This calculation was made by assuming infinitely narrow Bragg peaks; now, given that the apparent domain size is quite large (in the micron range), we can neglect this contribution as the peak width will be << 0.6 deg. Even the observed peak width (probably then dominated by the capillary size projection) is << 0.6 deg, so even if the apparently large domains are split in smaller coherent regions, this split is not so fine as to increase the estimate of the off-plane angular acceptance.

Having a total of a few thousands illuminated grains in the sample volume, this makes the number of contributing grains to each Bragg peak in the order of at most a few tens, even considering the Bragg multiplicity. And this is not enough to give a statistically consistent profile.