Supporting Information

Overlooked Impact of Surface Hydroxylation on the Solubility of Less-Soluble Compounds: A Case Study of CeO_2

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KEYWORDS Cerium, oxide, nanoparticles, solubility, kinetics, surface, hydroxylation.

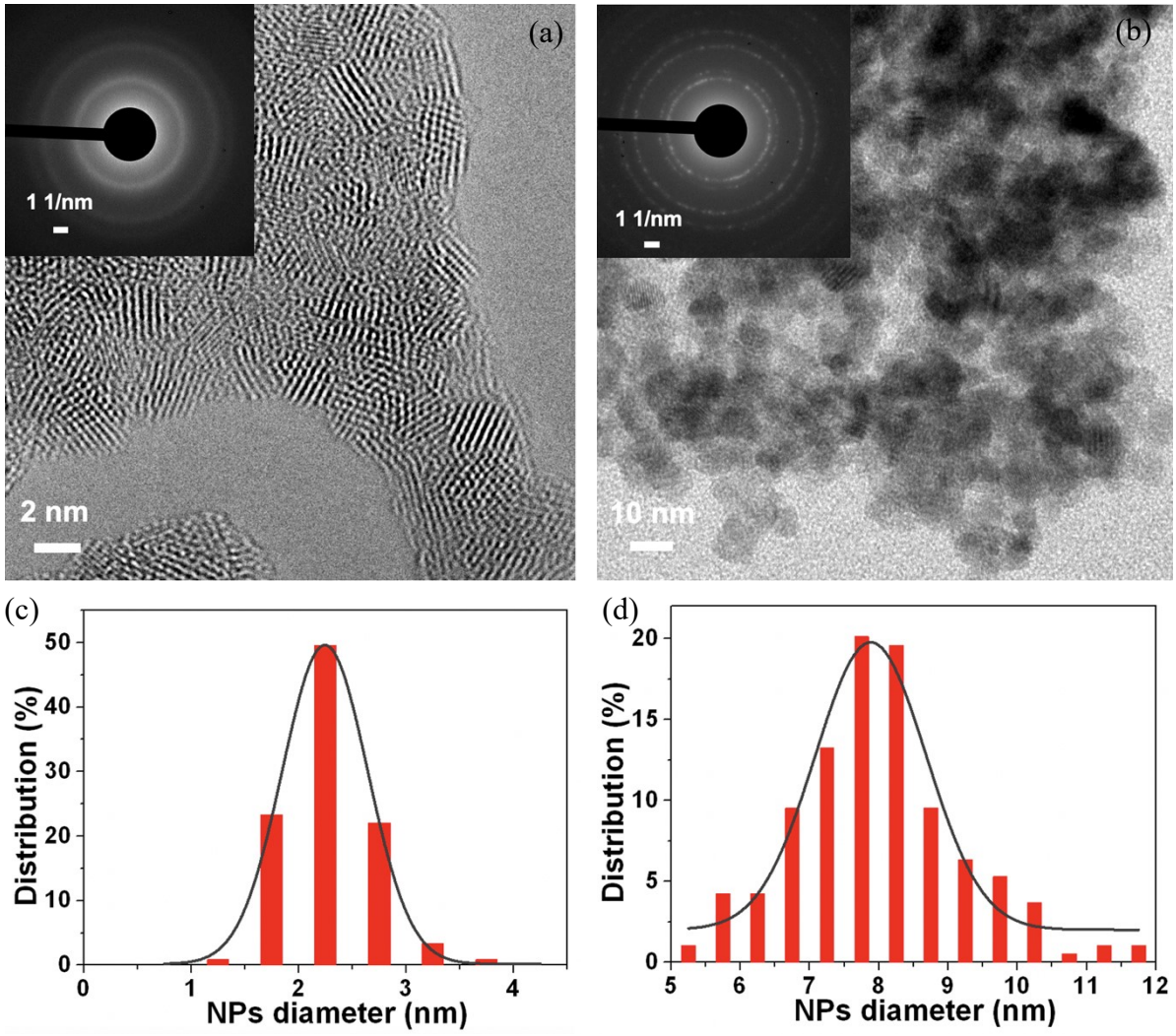

Fig. S1. HRTEM images and ED data (insets) for non-treated ceria samples synthesised from (a) 0.001M and (b) 0.8M cerium(III) nitrate solutions by chemical precipitation with 3M aqueous ammonia solution. Particle size distributions (c, d) were obtained from HRTEM data.

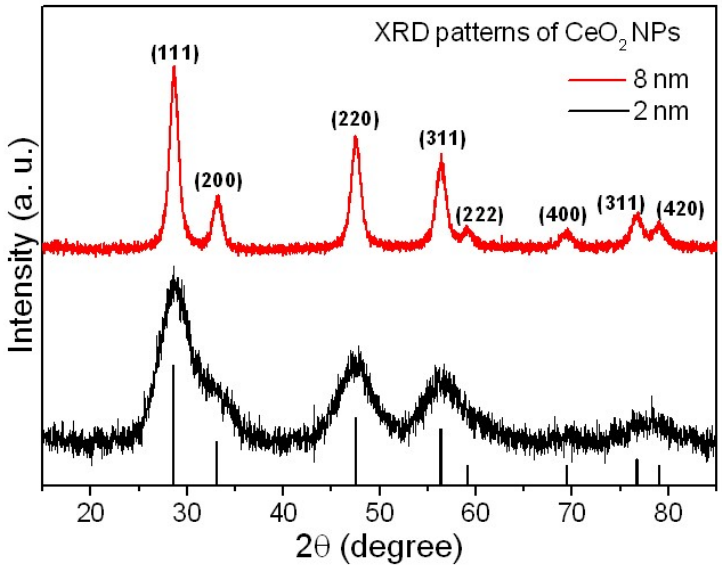

Fig. S2. Powder XRD patterns for ceria samples. Data collected using laboratory diffractometer (λ=1.54 Å).

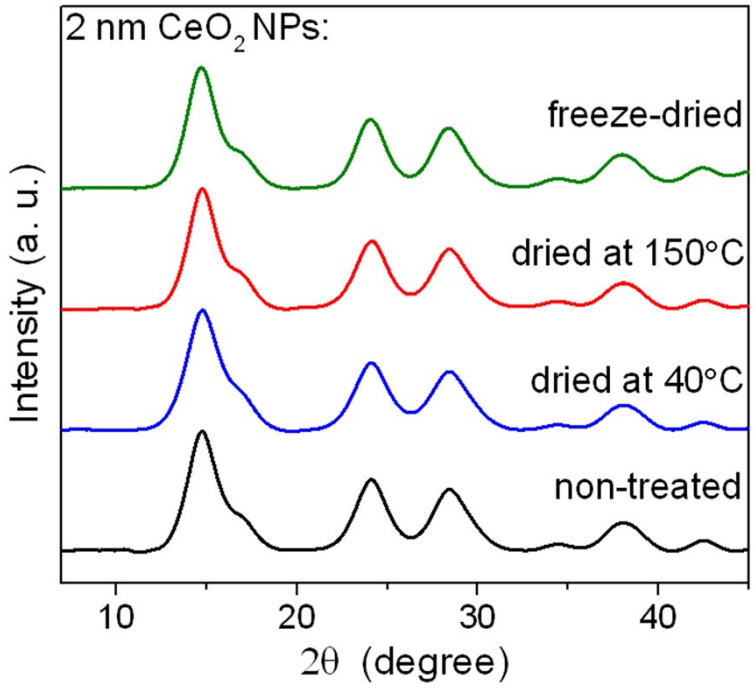

Fig. S3. XRD (λ = 0.8 Å) data for non-treated CeO_2 NPs and the samples after drying under different conditions. Data collected at the Kurchatov Synchrotron Radiation Source.

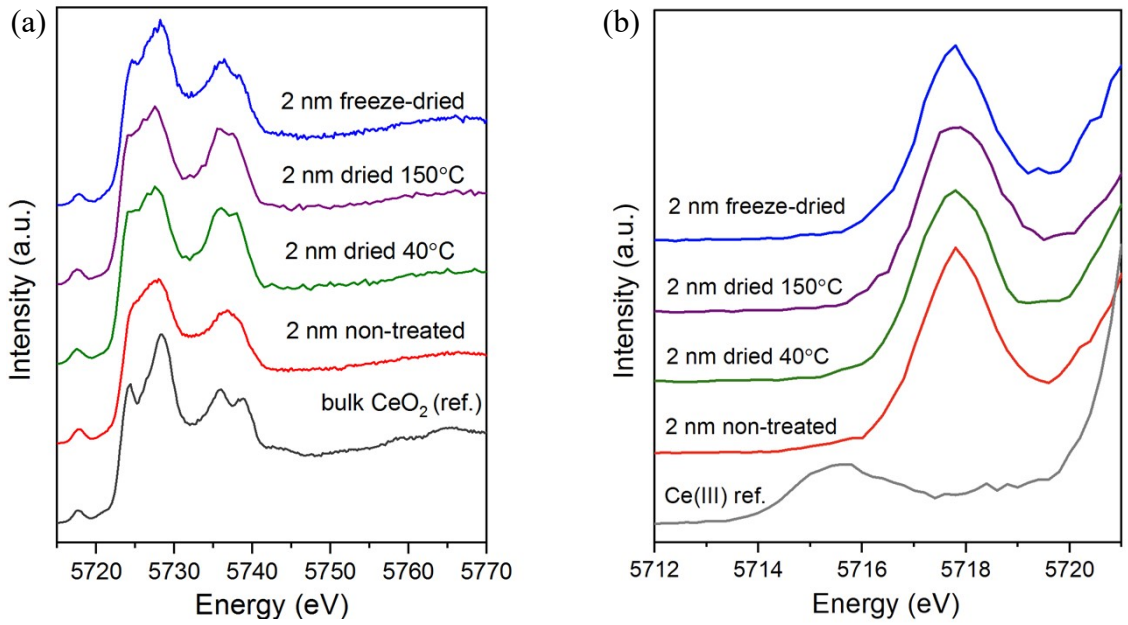

Fig. S4. (a) Ce L_3 edge HERFD-XAS data for CeO_2 2 nm samples ((b) shows an enlarged pre-edge region). CeO_2 bulk was used as a Ce(IV) reference and $Ce_2(SO_4)_3$ was used as a Ce(III) reference. The shape and position of the pre-edge features in CeO_2 samples indicate the absence of Ce(III) in NPs' structure before and after drying.

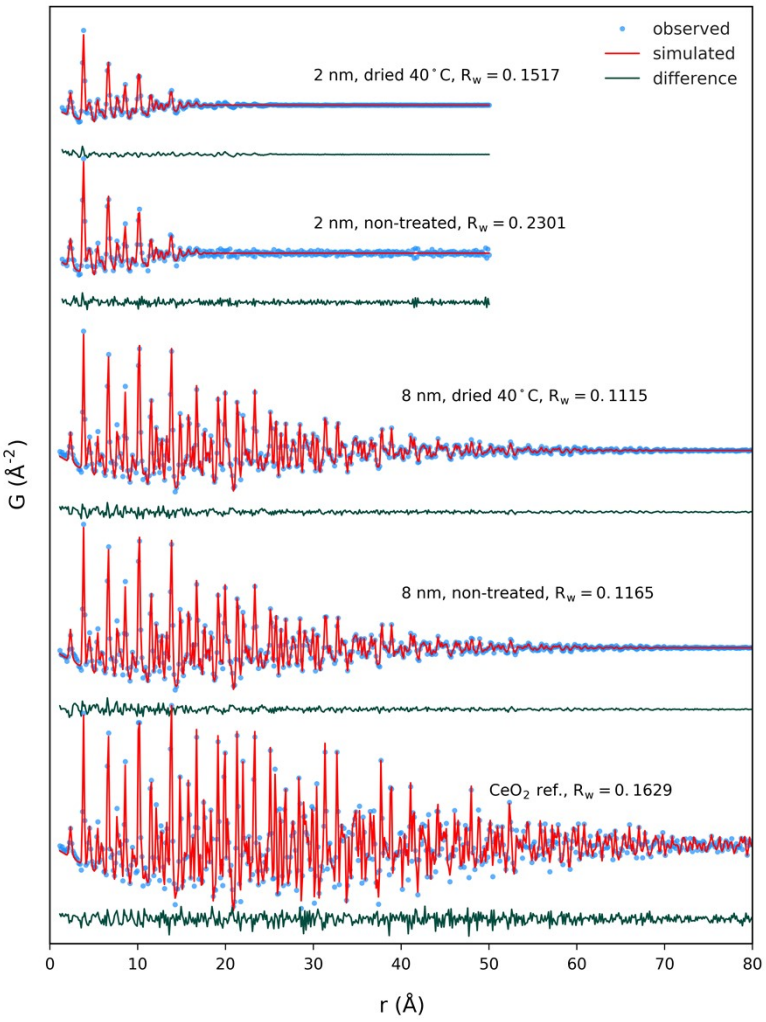

Fig. S5. PDF G(r) experimental data for CeO_2 NPs and CeO_2 reference samples compared with the fit results.

Table 1S: Refined parameter values derived from crystal structure refinement of CeO_2 to the local structure in the PDF data from the 2 nm and 8 nm samples non-treated or dried at 40°C, and the reference sample. *Dc* is the size of the coherent structural domain of the crystallites, as estimated from a spherical domain approximation. Uncertainties reflect the precision in the fitting of the model, and were estimated by refinement of the data on a Nyquist grid, i.e., $\Delta r = \pi/Q_{max}$.

	2 nm non-treated	**2 nm dried 40°C**	**8 nm non-treated**	**8 nm dried 40°C**	**Reference**
Ref. range / Å	1.0 - 50.0	1.0 - 50.0	1.0 - 80.0	1.0 - 80.0	1.0 - 80.0
a / Å	5.4157(19)	5.4133(10)	5.42408(17)	5.42271(16)	5.41374(13)
Uiso(Ce) / Å^2	0.0114(5)	0.0124(3)	0.00709(9)	0.00728(9)	0.00473(8)
Uiso(O) / Å^2	0.059(6)	0.067(4)	0.0395(15)	0.0398(15)	0.0198(10)
δ1	1.51(13)	1.69(7)	1.50(6)	1.55(6)	0.83(15)
Dc / Å	20.2(3)	20.6(2)	84.3(1.2)	85.3(1.2)	-
R_w	0.2301	0.1517	0.1165	0.1115	0.1629

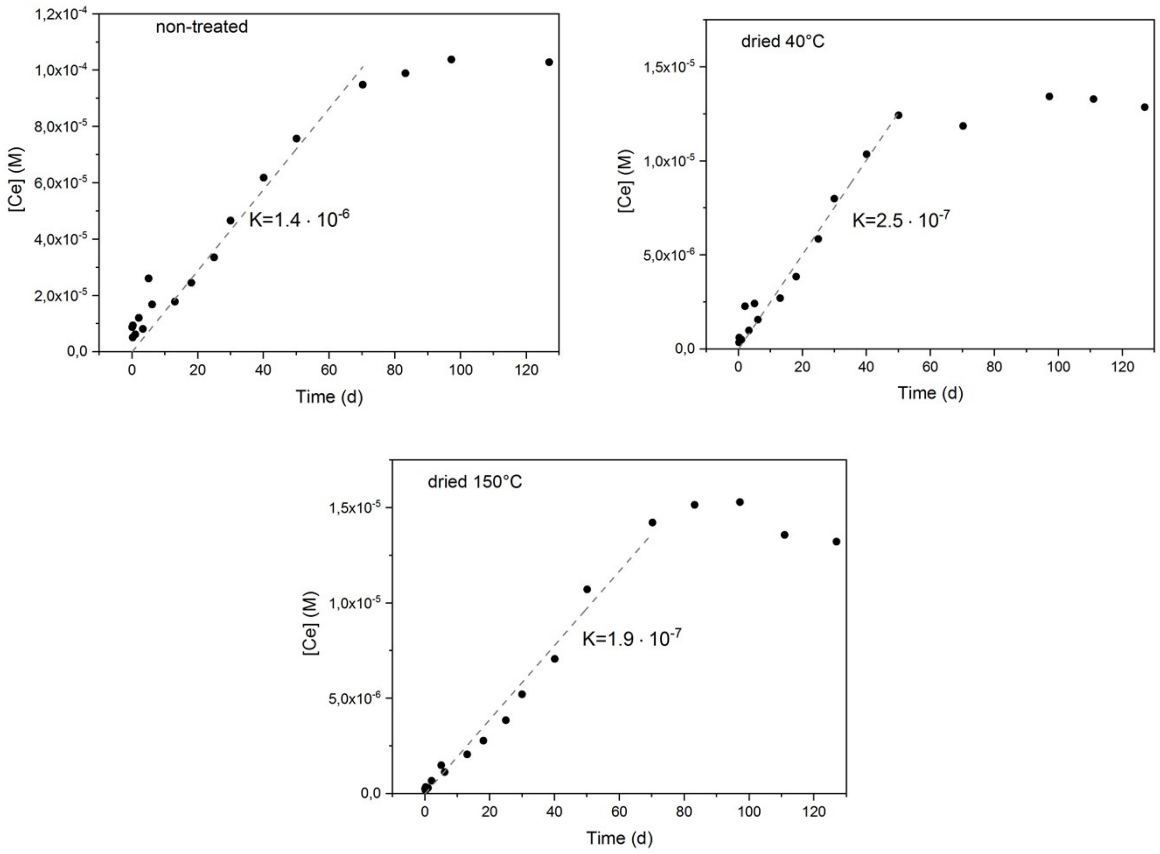

Fig. S6. CeO_2 2 nm dissolution curves in C(t) coordinates.

Table S2: Dissolution rate constants, calculated from experimental data on CeO_2 NPs' dissolution kinetics under pH = 4.1 ± 0.2.

System	Rate constant, mol/(L·day)
CeO_2 2 nm non-treated	$1.4 \cdot 10^{-6}$
CeO_2 2 nm dried 40°C	$2.5 \cdot 10^{-7}$
CeO_2 2 nm dried 150°C	$1.9 \cdot 10^{-7}$
CeO_2 8 nm non-treated	$2.8 \cdot 10^{-6}$
CeO_2 8 nm air-dried 40°C	$5.9 \cdot 10^{-7}$
CeO_2 8 nm air-dried 150°C	$6.6 \cdot 10^{-7}$

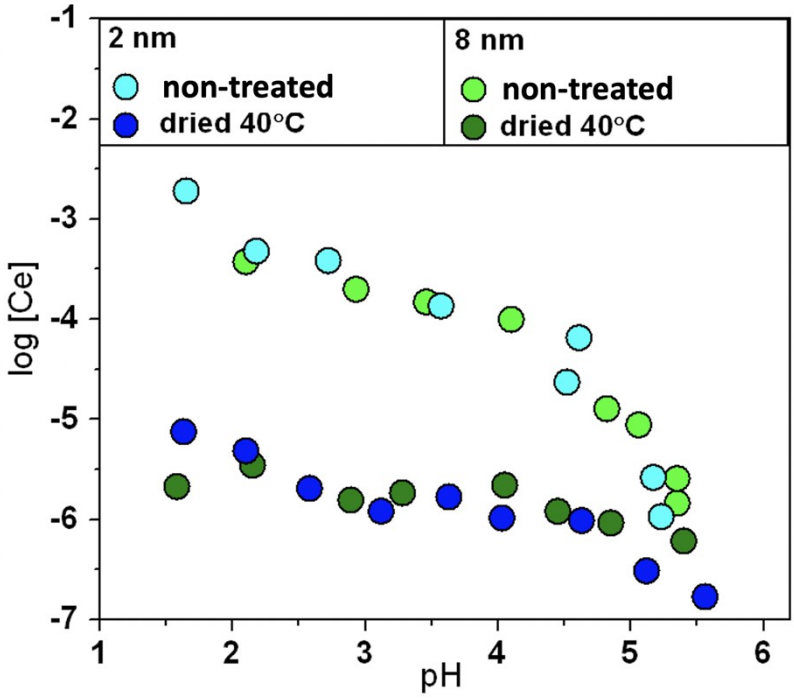

Fig. S7. Experimental data for CeO_2 NPs' solubility of 2 and 8 nm size, before and after heat treatment.

CeO_2 NPs after interaction with solution:

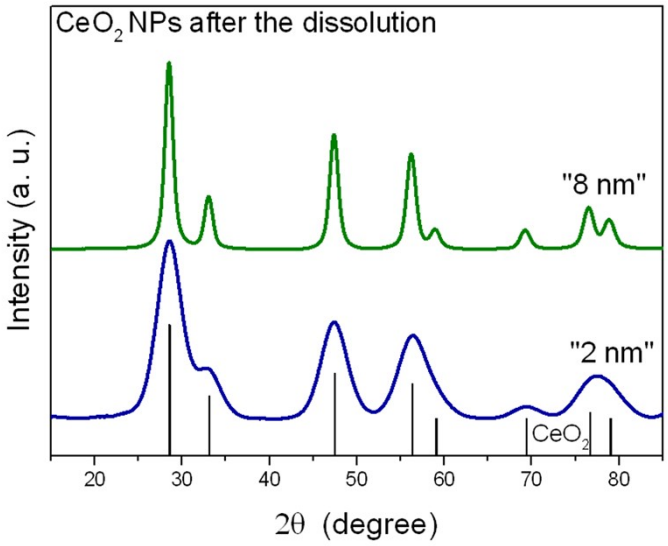

Fig. S8. XRD data for non-treated CeO_2 NPs of different sizes after long-term (4.5 years) interaction with solution at pH = 4. The phase composition and crystalline size remained unchanged within this time period.

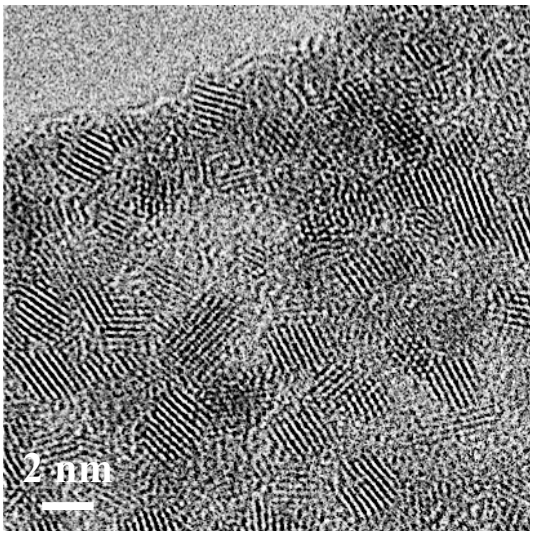

Fig. S9. HRTEM results of the non-treated 2 nm CeO_2 sample after 200 days of contact between the solid phase and an aqueous solution. Particle morphology remained unchanged during this time.

Table 3S: Comparison of cerium concentration in solution after centrifugation at different speeds.

Sample	Centrifugation type	Dissolved cerium concentration, M
CeO_2 2 nm non-treated pH = 2.2	High-speed long-term (64 000 g, t = 4 h)	$(7.8 \pm 0.8) \cdot 10^{-4}$
CeO_2 2 nm non-treated pH = 2.2	Ultracentrifugation (300 000 g, t = 30 min)	$(7.1 \pm 0.7) \cdot 10^{-4}$
CeO_2 2 nm non-treated pH = 1.7	High-speed long-term (64 000 g, t = 4 h)	$(3.8 \pm 0.4) \cdot 10^{-3}$
CeO_2 2 nm non-treated pH = 1.7	Ultracentrifugation (300 000 g, t = 30 min)	$(3.0 \pm 0.3) \cdot 10^{-3}$
CeO_2 2 nm non-treated pH = 4.2	High-speed long-term (64 000 g, t = 4 h)	$(2.0 \pm 0.2) \cdot 10^{-4}$
CeO_2 2 nm non-treated pH = 4.2	Ultracentrifugation (300 000 g, t = 30 min)	$(2.0 \pm 0.2) \cdot 10^{-4}$