

Supporting information

Towards the surface hydroxyl species in CeO₂ nanoparticles

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Figure S1 describes schematically the main principles of HERFD-XAS and soft XAS experiments as applied in studies of CeO₂ NPs. The absorbed photons cause excitation of the inner shell electrons of the atoms in the material. These excited inner shell (core) electrons can be promoted to unoccupied energy levels to form a short-lived excited state. CeO₂ soft XAS spectrum shows peaks in M₅ region. The peaks, which occur at the energies 883.6 and 888.6 eV, are attributed to the transitions from 3d_{5/2} to 4f states. At the Ce L₃ edge, the electrons are excited from the 2p to 5d states due to the dipole transitions. Pre-edge Ce L₃ edge structure is attributed to the quadrupole 2p to 4f states.

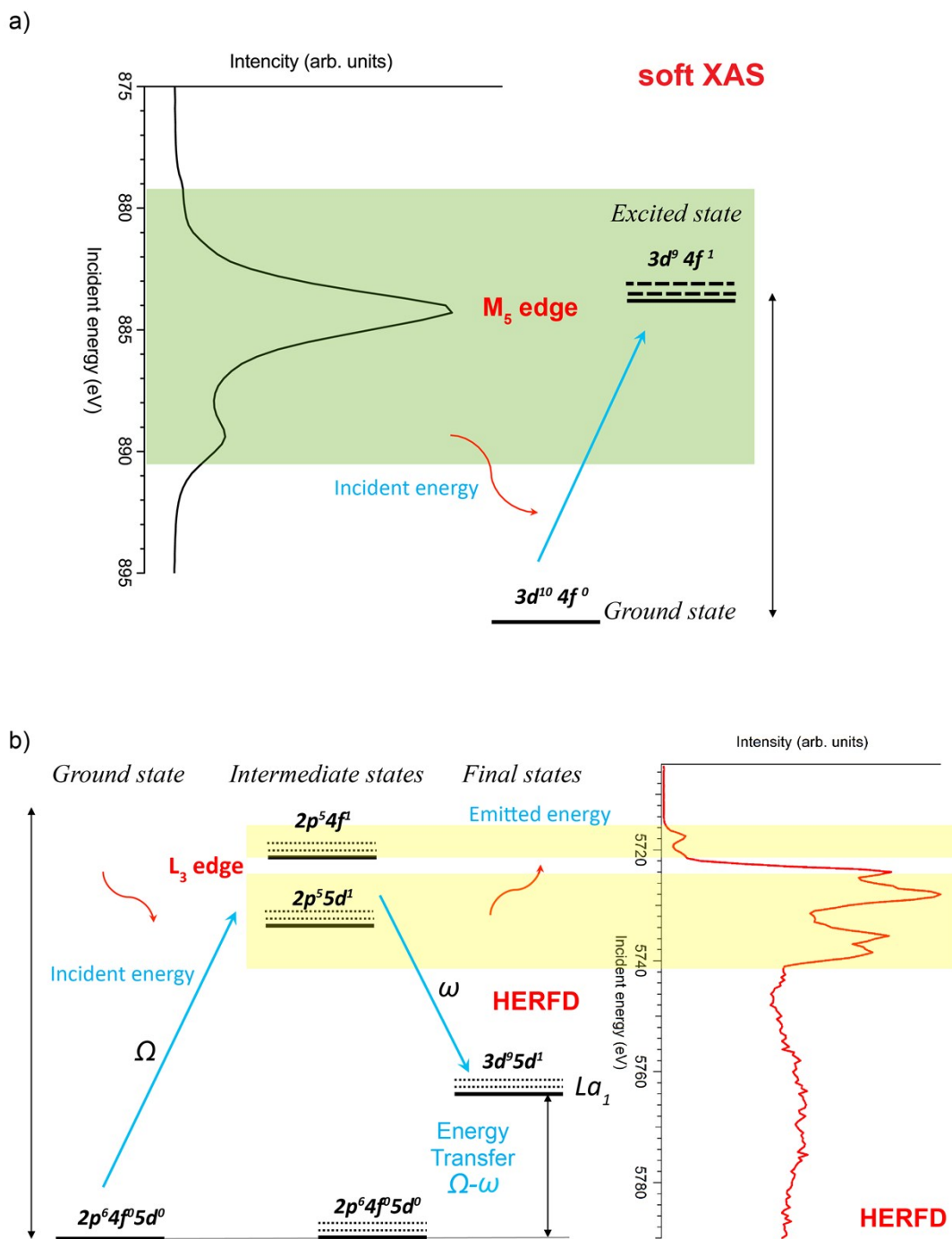


Figure S1. Schematic of a) HERFD-XAS and b) soft XAS techniques.

Figure S2 shows results of the powder XRD analysis for ceria NPs samples. XRD has shown that all samples are of a single phase and correspond to cubic CeO₂ (PCPDF 81-792), that confirms the electron diffraction data obtained from the same samples. The particle size of nanocrystalline ceria (D) from XRD data was calculated using the Scherrer equation (1):

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl} \cos(\theta)}, \quad (1)$$

where λ is the wavelength (0.15 nm); K is the coefficient of anisotropy that is generally set to be 1.0 for spherical particles; θ is the scattering angle in radians; β_{hkl} is full width at half-maximum (FWHM) for diffraction peak expressed in radians. Line profiles for (111) and (200) reflections were fit to pseudo-Voigt functions. Particle size was calculated from FWHM of (111) and (200) diffraction lines. Instrumental broadening was taken into account when calculating the particle size by direct subtraction from the FWHM values. Instrumental broadening for the laboratory XRD equipment was considered to be 0.09 ± 0.01 °2 θ . Particle size calculated using Scherrer formula was 2.5 nm for CeO₂ prepared from 0.001M Ce(NO₃)₃, 5.5 nm for CeO₂ prepared from 0.1M Ce(NO₃)₃ and 8.8 nm for CeO₂ prepared from 0.8M Ce(NO₃)₃.

HRTEM images (Fig. S3) show that NPs are fairly uniform in size and mostly have a truncated octahedral shapes. This is in agreement with previously published data from a computer simulations¹. Electron diffraction patterns for the analyzed samples confirm a fluorite crystal structure. To obtain the average size and distribution from HRTEM images, the calculation of diameters for more than 200 particles were conducted. The measured size distributions are plotted in Figure S3 d), e), and f). All three samples show relatively small polydispersity, and their size distributions can be fitted well by a Gaussian function. Average NPs diameter were 2.3 ± 0.4 , 5.9 ± 1.1 and 7.8 ± 1.2 for samples synthesized from 0.001M, 0.1 M and 0.8 M Ce(NO₃)₂ respectively. The increase in NPs size with an increase in concentration of initial cerium (III) salt is consistent with previous studies. This fact is usually attributed to the presence of an intermediate stage formation of cerium hydroxide (III)². The crystallite size determined from the XRD data is in a good agreement with the average size found from HRTEM data.

SAXS curves were recorded for ceria NPs samples are reported in Fig. S4. Volume size distributions for NPs were calculated from these curves by the GNOM program³. The average particle size was 2, 4 and 8 nm for samples synthesized from 0.001M, 0.1 M and 0.8 M Ce(NO₃)₂ correspondingly.

Based on results presented in Fig. S2, S3 and S4, samples are marked as “2 nm” for CeO₂ prepared from 0.001M Ce(NO₃)₃, “5 nm” for CeO₂ prepared from 0.1M Ce(NO₃)₃ and for “8 nm” for CeO₂ prepared from 0.8M Ce(NO₃)₃.

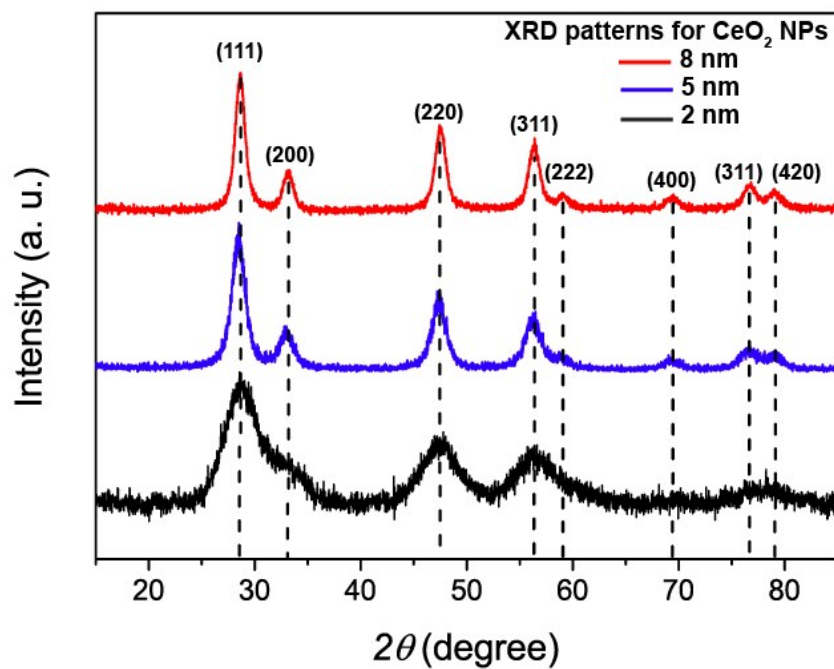


Figure S2. Powder XRD patterns for ceria NPs samples.

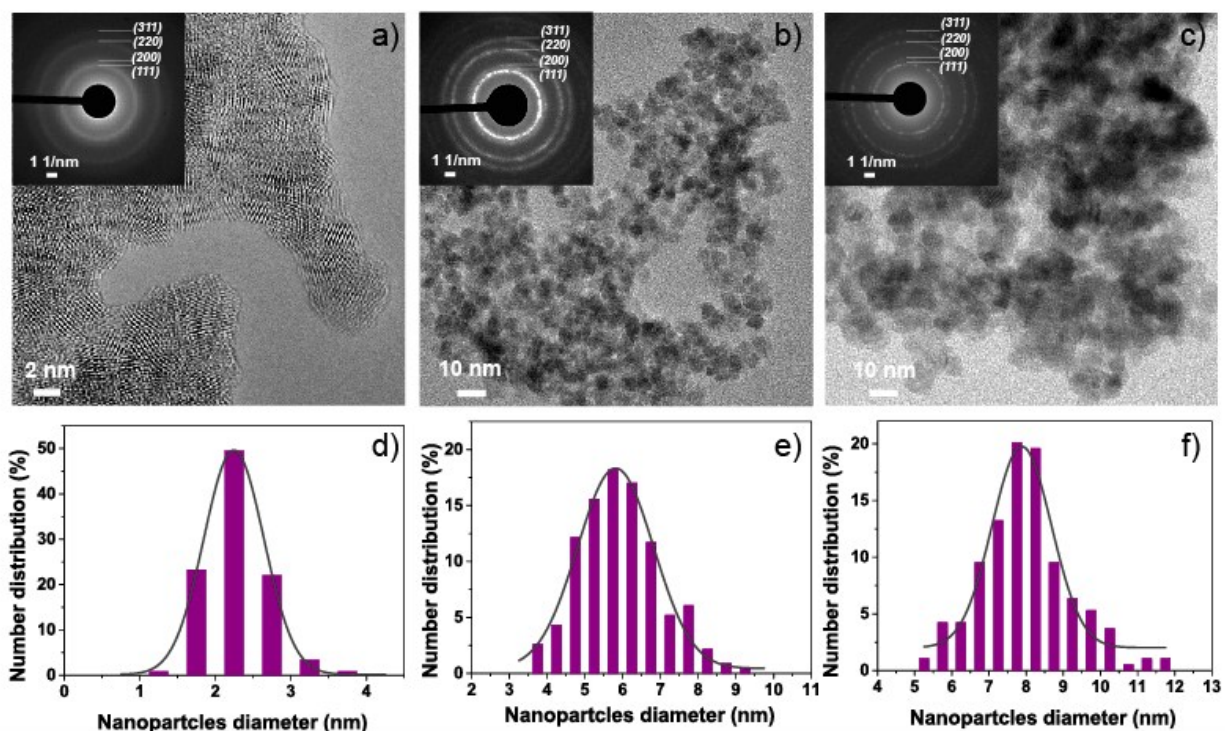


Figure S3. HRTEM images and size distributions from HRTEM for the CeO₂ NPs samples.

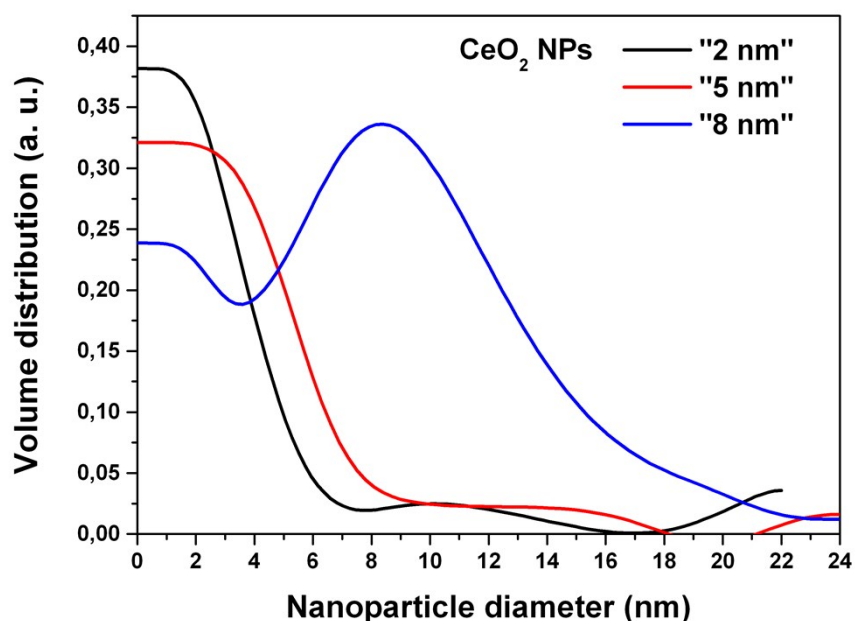


Figure S4. NP size distribution calculated from SAXS data using GNOM program ³.

Figure S5 shows HERFD-XAS pre-edge spectra at the Ce L_3 edge of CeO₂ NPs (2, 5 and 8 nm) in different states (as prepared and after the heat treatment) compared to the spectra of Ce(III) and Ce(IV) reference materials. The HERFD-XAS spectra recorded by monitoring the maximum of $L\alpha_1$ ($3d_{5/2}-2p_{3/2}$) intensity as a function of incident energy. The advantage of such a setup is two-fold: the width of the spectral features is no longer limited by the $2p_{3/2}$ core hole lifetime but the sharper $3d_{5/2}$ core hole width in the final state. Furthermore, electron–electron interactions in the final state between the 3d hole and 4f electrons can be observed that provide valuable information on the 4f electron configuration.

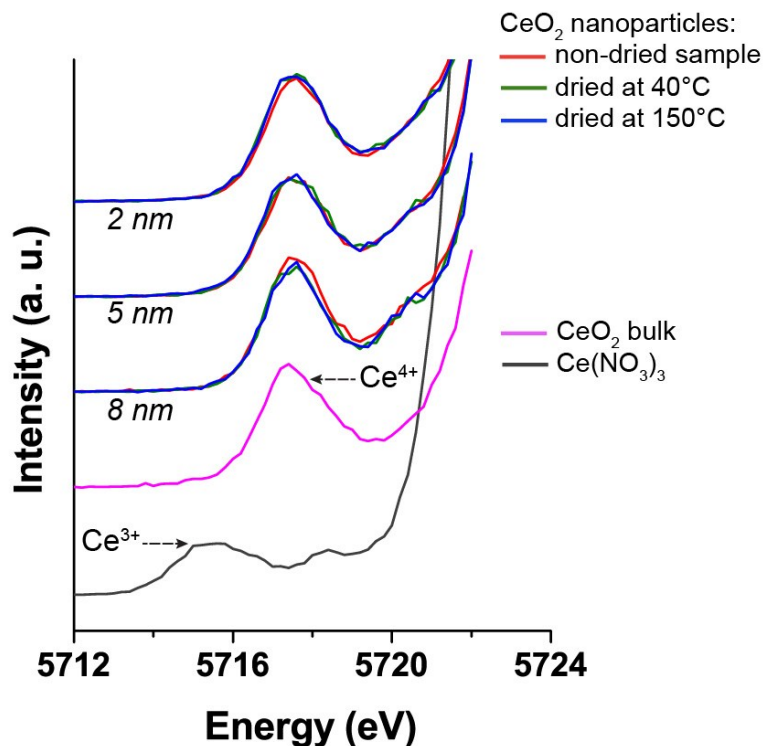


Figure S5. Pre-edge HERFD-XAS spectra for CeO₂ bulk material, cerium nitrate and for NPs studied in the present work.

In our previous studies, the pre-edge transitions below the absorption edge are attributed to the excitations into the 4f states⁴. A Ce(IV) compound formally contains no 4f electrons in the ground state and one 4f electron in the XAS final state. The CeO₂ HERFD-XAS spectrum shows a single peak at 5717.5 eV in the pre-edge region. When the number of 4f electrons in the final state is increased to two for Ce(III) the spectral shape becomes broader. In that case the number of contributing states is increased due to electron–electron interactions in the 4f valence orbital and the pre-edge profile becomes more complicated. The transitions to these states are split in two groups (Fig. S5 bottom, spectrum of Ce(NO₃)₃).

The present results show that pre-edge HERFD-XAS structure in spectra of CeO₂ NPs (in different size and at different conditions – treated under various temperatures) exhibit only single profile, confirming the presence of only Ce(IV) oxidation state.

The synchrotron XRD patterns of “2 nm” sample collected after the synthesis and after thermal treatment at 40 °C and 150 °C are shown in Fig. S7. All diffraction peaks can be attributed to the CeO₂ phase. The peaks position and its broadening do not change after the thermal treatment of the NPs samples. To support the XRD data, electron diffraction patterns were collected during HRTEM measurements of “as-prepared” 2 nm sample, and the same samples after 40

°C temperature treatment (Fig. S8). The electron diffraction results confirm the phase stability of the studied samples. According to the HRTEM images analysis, an average NP size for “as-prepared” and dried sample is established to be 2.3 ± 0.4 .

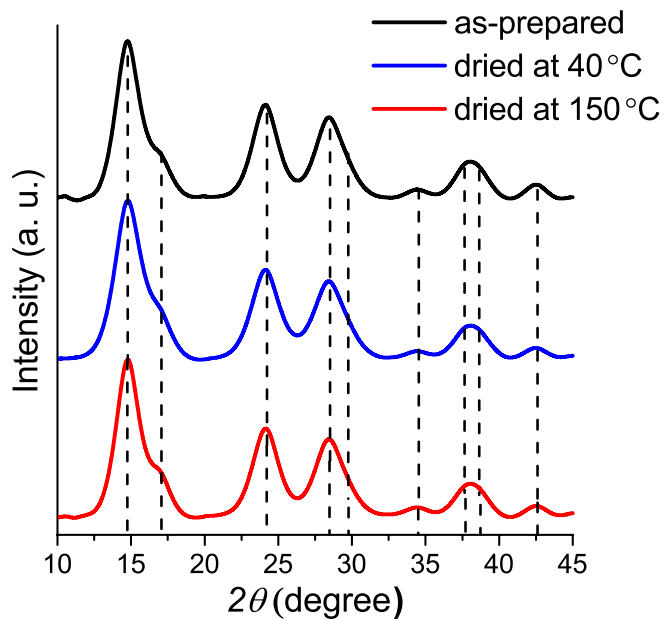


Figure S6. Synchrotron XRD data for as-prepared and dried at 40 °C and 150 °C CeO_2 samples.

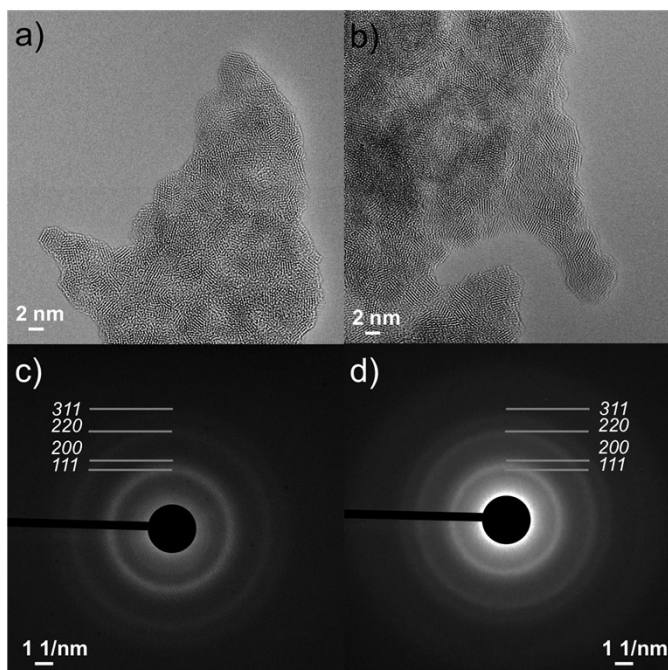


Figure S7. HRTEM data and electron diffraction patterns for CeO_2 samples a) c) as-prepared and b) d) dried at 40 °C.

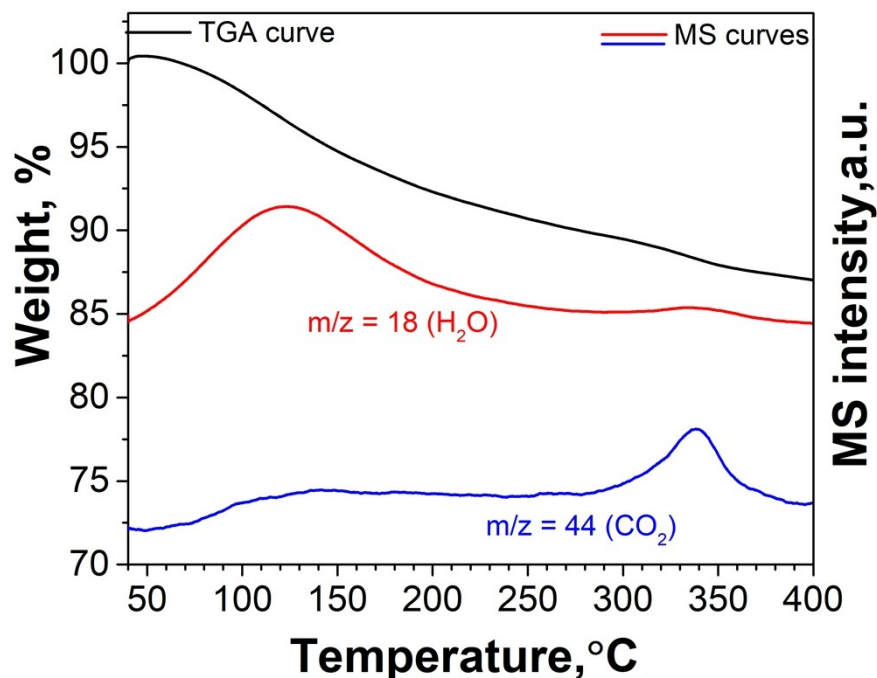


Figure S8. Thermogravimetric analysis (TGA) data and the corresponding mass spectral data for H₂O (MW 18) and CO₂ (MW 44) evolution from CeO₂ NPs of 2 nm size. TGA curve for CeO₂ sample demonstrate 15% total weight loss during the heating process. The mass spectra of 2 nm sample contain peaks corresponding to H₂O and CO₂ evolution. The presence of water in the mass spectrum in the range of 40 – 200 °C indicates that the 2 nm CeO₂ sample contain the water sorbed on the surface as well as water trapped in the bulk.

Chemiluminescence kinetic measurements

Chemiluminescence (CL) techniques possess the highest sensitivity in determination of ROS scavenger ability of substances. In particular, the TRAP (Total Radical-Trapping Antioxidant Potential) method is widely used in practice. This method is based on the ability of substances to intercept free radicals formed during the decomposition of thermolabile compounds, for example, 2,2'-azobis (2-amidinopropane) (ABAP) ^{5, 6}. In the present study, the antioxidant activity of NPs was estimated using luminol (5-amino-1,2,3,4-tetrahydro-1,4-phthalazinedione) – by activated CL method ⁷. The CL kinetics was measured using Lum-100 luminometer (DiSoft, Russia). The operation of the device, the analysis of the results of photon counting, and plotting were performed using the Power Graph software. Measurements were conducted at 37°C. For the measurements, we used two different buffer solutions: the citrate buffer, pH 7.4 (30 mM trisodium citrate), and the phosphate buffer, pH 7.4 (100 mM potassium dihydrogen phosphate) both prepared using ultrapure water. Reagents were mixed directly in the CL cuvette. 50 µL of 0.05 M ABAP aqueous solution and 20 µL of 0.1 mM luminol in the

appropriate buffer solution were preincubated in the dark at room temperature for 20 min. Thermal decomposition of the radical source was triggered by adding the necessary amount of a preheated buffer solution (37°C) (Fig. S9, “step 1”). The final system volume was 1.0 mL. After the CL curve reached a plateau, an aliquot of the analyzed sample was injected into the system. In this way, the antioxidant activity of aqueous suspensions of freshly precipitated CeO₂ NPs with average sizes of 2 and 8 nm were analyzed. Suppression of luminescence due to radical scavenger ability of both samples was clearly. At the next step (Fig. S9), CL intensity increased with time. Under the chosen experimental conditions, the registration of kinetics was continued until the system reached the stationary mode (“step 3” on Fig. S9). The antioxidant activity of the samples was evaluated by measuring the area under the CL curve in the range corresponding to step 2. For each system measurement were made three times.

CL of the ABAP–luminol system was recorded in a control experiment. Addition of pure phosphate buffer exerted no effect on the curve shape. In the case of citrate buffer, the slight antioxidant effect was registered. This contribution was taken into account when evaluating the antioxidant activity of CeO₂ NPs samples in citrate buffer. Estimated antioxidant activity of the samples was expressed in equivalent units of a water-soluble analog of vitamin E, Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid).

According to CL kinetic curves for citrate and phosphate buffer solutions (Fig. S9a and Fig. S9b correspondingly), 2 nm CeO₂ NPs possess higher antioxidant activity in comparison with 8 nm CeO₂ NPs. The estimated value of antioxidant activity for 8.6 mg/L colloid solution of 2 nm CeO₂ NPs in citrate buffer was found to be 0.23 ± 0.07 μM in Trolox units, and 0.04 ± 0.01 μM in Trolox units for 8 nm CeO₂ NPs sample of the same concentration.

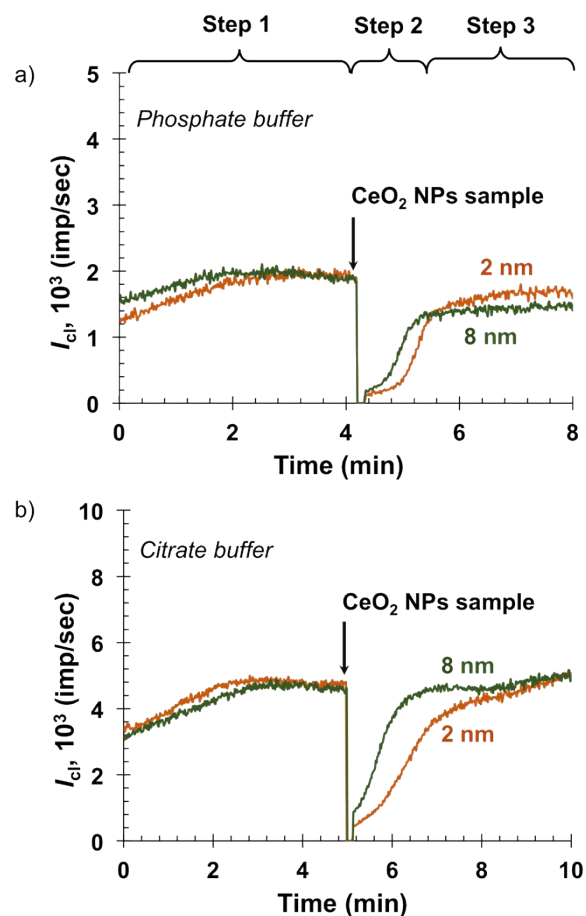


Figure S9. The CL curves of the ABAP (2.5 μ M) + luminol (2.0 μ M) a) in phosphate buffer (100 mM, pH 7.4), and b) in citrate buffer (30 mM pH 7.4) containing 2 nm and 8 nm CeO₂ NPs (8.6 mg/L). Total system volume is 1.0 mL.

References

1. T. X. T. Sayle, S. C. Parker and D. C. Sayle, *Chem. Commun.*, 2004, 2438-2439.
2. L. Yin, Y. Wang, G. Pang, Y. Koltypin and A. Gedanken, *J. Colloid Interface Sci.*, 2002, **246**, 78-84.
3. D. I. Svergun, *J. Appl. Crystallogr.*, 1992, **25**, 495-503.
4. K. O. Kvashnina, S. M. Butorin and P. Glatzel, *J. Anal. At. Spectrom.*, 2011, **26**, 1265-1272.
5. E. A. Lissi, C. P. Pascual and M. D. Castillo, *Free Radic. Res. Commun.*, 1992, **17** 5, 299-311.
6. E. Lissi, M. Salim-Hanna, C. Pascual and M. D. Castillo, *Free Radical Bio. Med.*, 1995, **18**, 153-158.
7. A. V. Alekseev, E. V. Proskurnina and Y. A. Vladimirov, *Moscow Univ. Chem. Bull.*, 2012, **67**, 127-132.