Electronic Supplementary Material (ESI) for RSC Advances

SUPPLEMENTARY INFORMATION

Aminopolycarboxylic Acids as a Versatile Tool to Stabilize Ceria Nanoparticles – A Fundamental Model Experimentally Demonstrated

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Synthetic strategy

The synthetic steps of the ceria nanoparticles needed to be designed correctly in order to obtain a suitable size and size distribution of the formed particles. For instance, reduction of the ionic strength was carried out by removal of the supernatant from the cerium hydroxide cake by centrifuging, decanting and then re-dispersing it in water. The NTA solution was neutralized prior its addition to the cerium hydroxide dispersion, not to drop the pH and thus to avoid dissolution of the cerium hydroxides. The neutralization was carried out by addition of NH_4OH*. The* H_2O_2 *solution was added all at once to favor nucleation over growth and thus give small particles of narrow size distribution. An elevated temperature was needed for the crystallization of the oxides since lower temperatures were expected to originate higher degrees of amorphousness[1].*

The role of the H_2O_2 *is to oxidize* $Ce(OH)_3$ *to* $Ce(OH)_4$ *(which later evolves to* $CeO_2{\cdot}xH_2O$*). According to Djuricic and Pickering[2] and Lee and Choi[3], the oxidation of* $Ce(OH)_3$ *goes through an intermediate stage consisting of* $Ce(OH)_x(OOH)_{4-x}$ *which finally yields cerium (IV) oxide.*

[1] V. Briois, Journal of Materials Science, 28 (1993) 5019-5031.

[2] B. Djuričić, S. Pickering, Journal of the European Ceramic Society, 19 (1999) 1925-1934.

[3] J.-S. Lee, S.-C. Choi, Materials Letters, 58 (2004) 390-393.

XRD Studies

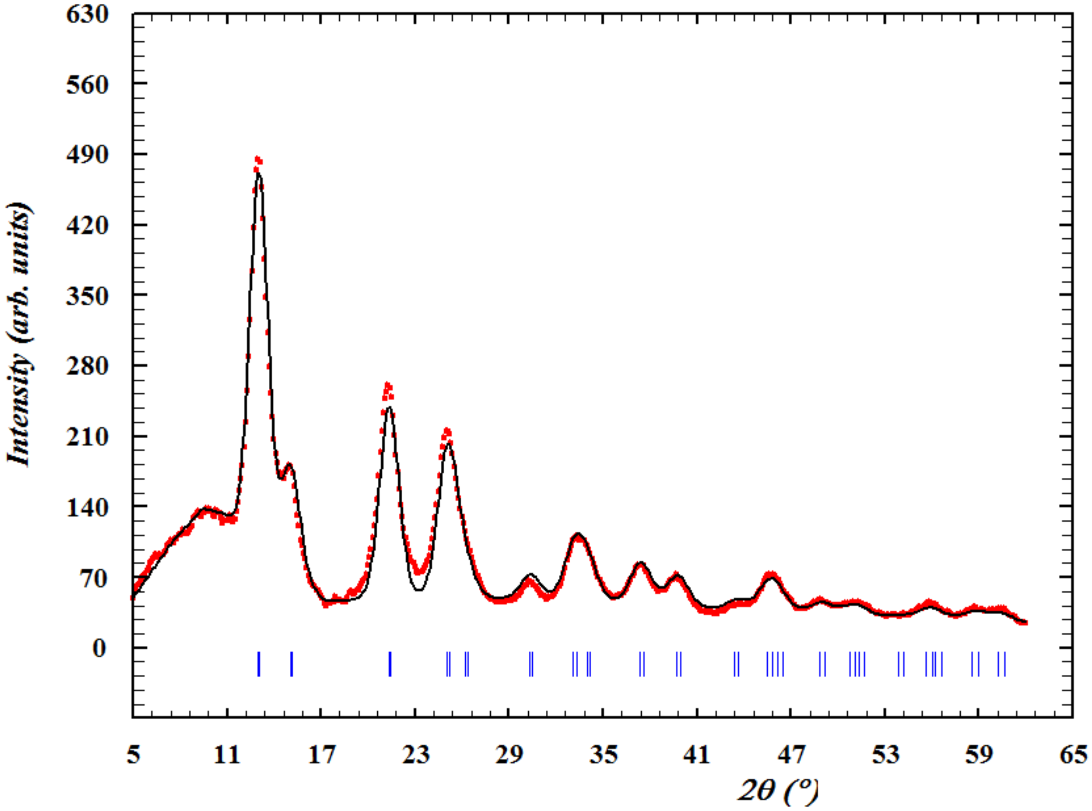

Figure S.1. X-ray diffraction in capillary of the NTA-stabilized ceria dispersion as synthesized. The pattern was recorded on Agilent Xcalibur diffractometer with molybdenum Kα_1 and Kα_2 radiation. The red dots correspond to the measured pattern. The black line shows the calculated pattern from the Rietveld refinement (RF-factor of 6.50). The blue vertical lines show the calculated peak positions for ceria.

XPS Study

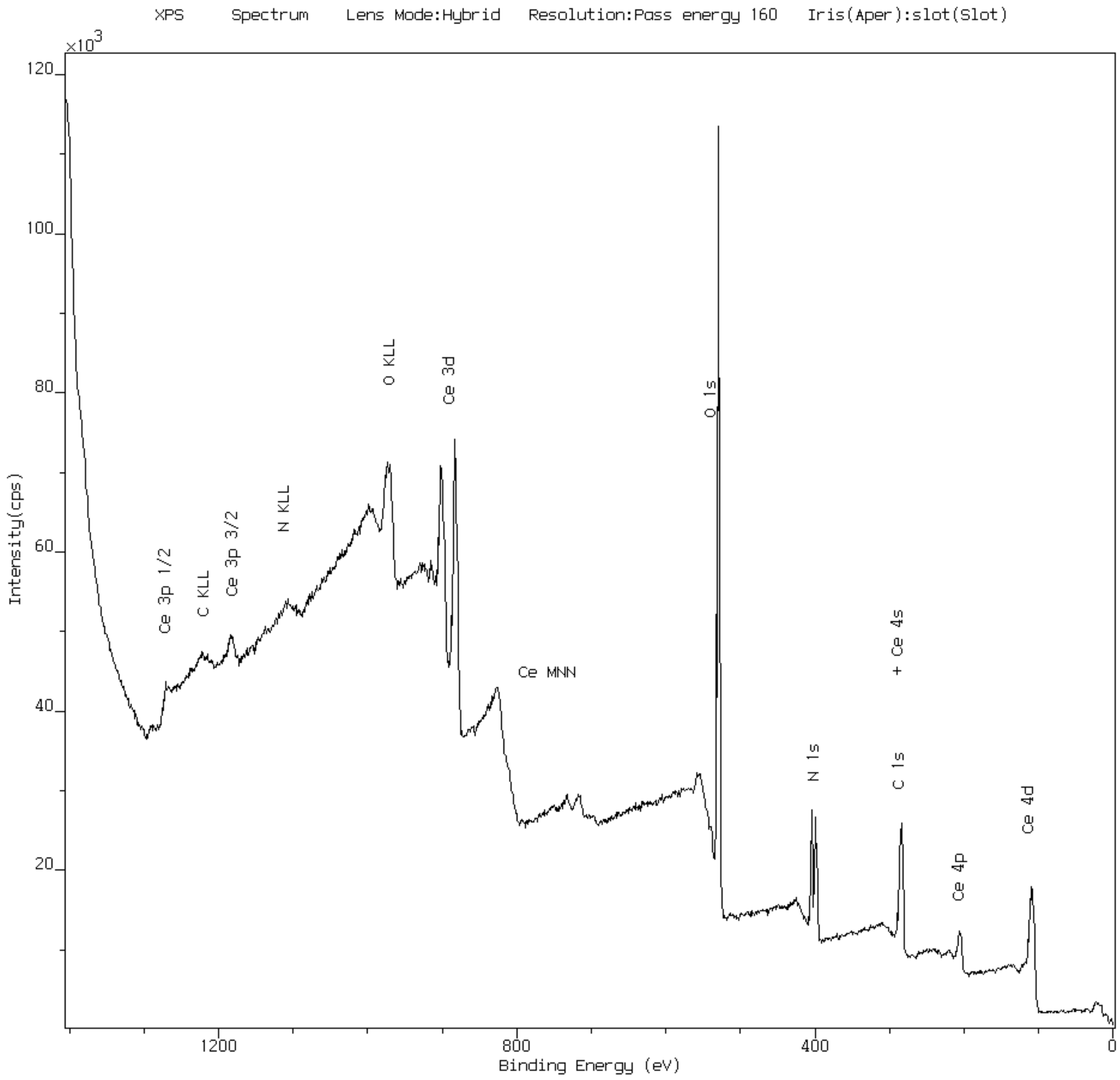

Figure S.2. Wide angle X-ray photoelectron spectrum of NTA-stabilized CeO_2 nanoparticles.

The spectrum was recorded using a Kratos AXIS Ultra^{DLD} x-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK). The sample was analyzed using a monochromatic Al x-ray source. The analysis area was below about 1 mm^2, with most of the signal from an area of 700 x 300 µm. In the analysis, wide (survey) spectra were run to detect elements present in the surface layer.

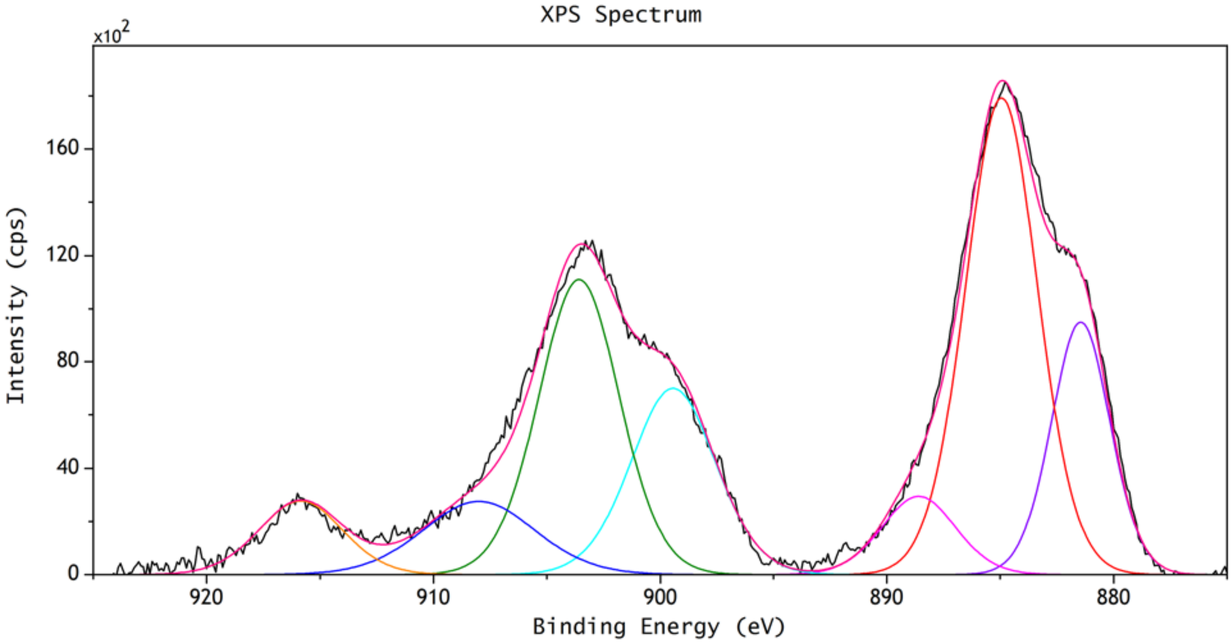

Figure S.3. X-ray photoelectron spectrum of NTA-stabilized CeO_2 nanoparticles.

The envelope curve shows the results obtained, the colored curves correspond to the curve-fitting peaks.

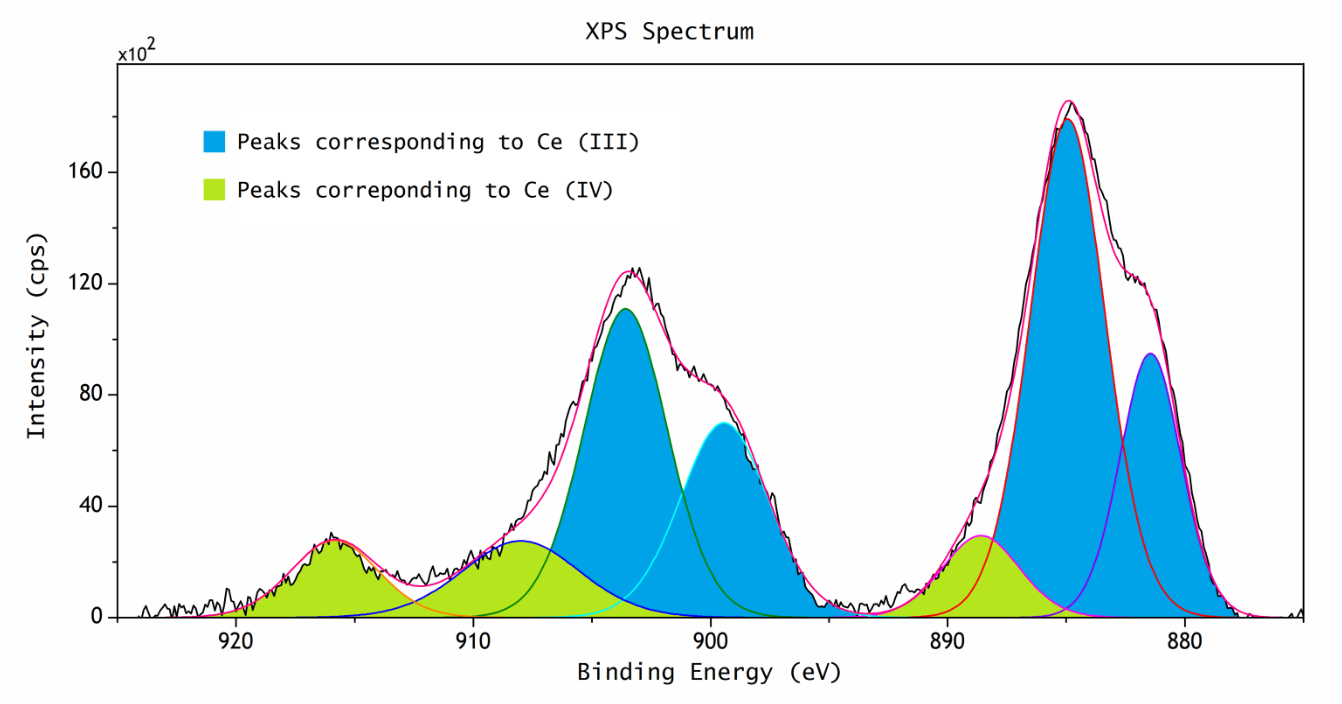

Figure S.4. XPS spectrum of NTA-stabilized CeO_2 nanoparticles, with peaks assigned to species.

The region of interest for cerium where the peaks corresponding to Ce (III) and Ce (IV) have been colored in blue and green, respectively. Peak assignment has been performed according to *Zhang et al. Surface Science 563 (2004) 74 – 82, Figure 1*.

The position and pattern of the bands in blue (four main peaks that appear in two pairs, being the one of lowest energy of each pair of lower intensity compared to the adjacent band on its left) correspond to Ce (III) in Ce_2O_3. The green bands do not fit with the Ce (III) profile; however they can be correlated to peaks characteristic of Ce (IV) in CeO_2.

We conclude that both Ce (III) and Ce (IV) are present on the sample surface. Since XPS is very surface sensitive, these results strongly indicate that the surface of NTA-stabilized CeO_2 nanoparticles consists predominantly of Ce (III).