

Electronic Supplementary Information

Determining the maximum lanthanum incorporation in the fluorite structure of La-doped ceria nanocubes for enhanced redox ability

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Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

TGA and DSC measurements were carried out on the dried samples using a Netzsch STA 409 PC, heating the samples from 25 °C to 600 °C at 10 °C/min, under a flow of air.

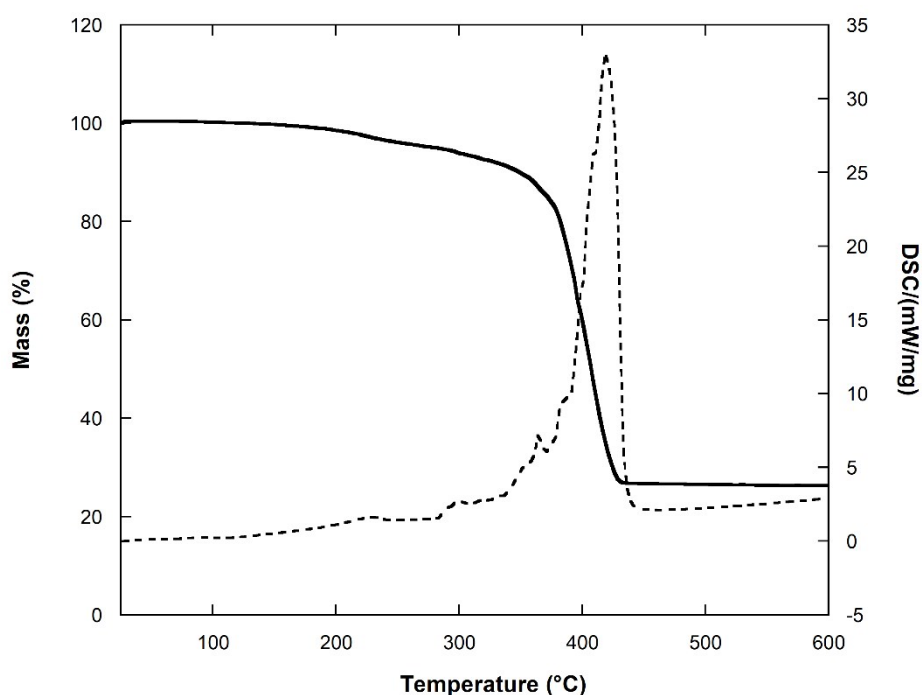


Fig. S1 TGA (continuous line) and DSC (dashed line) traces for undoped CeO₂ nanocubes.

Figure S1 shows the typical TGA and DSC traces that were obtained for all samples. A large amount, close to 80 wt%, of oleic acid is capping the particles which starts to decompose at temperatures above 200 °C. The main weight loss is close to 400 °C and is accompanied by a strong exothermic peak in the DSC due to the complete combustion of the oleic acid.

Powder X-ray Diffraction (XRD)

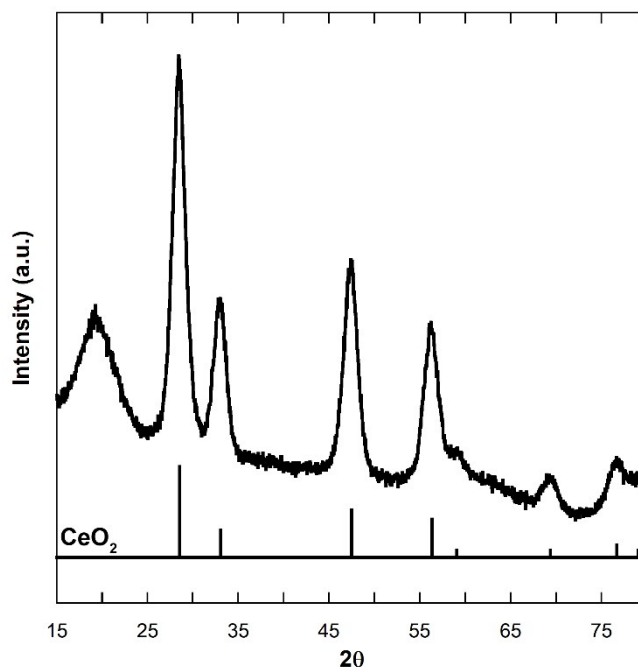


Fig. S2 XRD pattern obtained depositing undoped CeO₂ nanocubes as dried powder. The broad peak around 20° is due to the oleic acid.

The typical XRD pattern obtained for all the samples when deposited as dried powders is shown in Figure S2. All the peaks due to the CeO₂ fluorite structure appear with intensity ratios expected in absence of preferential orientations. A broad peak due to the capping agent is also evident with no sign of any additional impurities and/or other crystalline phases.

Spherical Aberration-Corrected Scanning Transmission Electron Microscopy - Energy Dispersive X-ray Spectroscopy (AC-STEM-EDS)

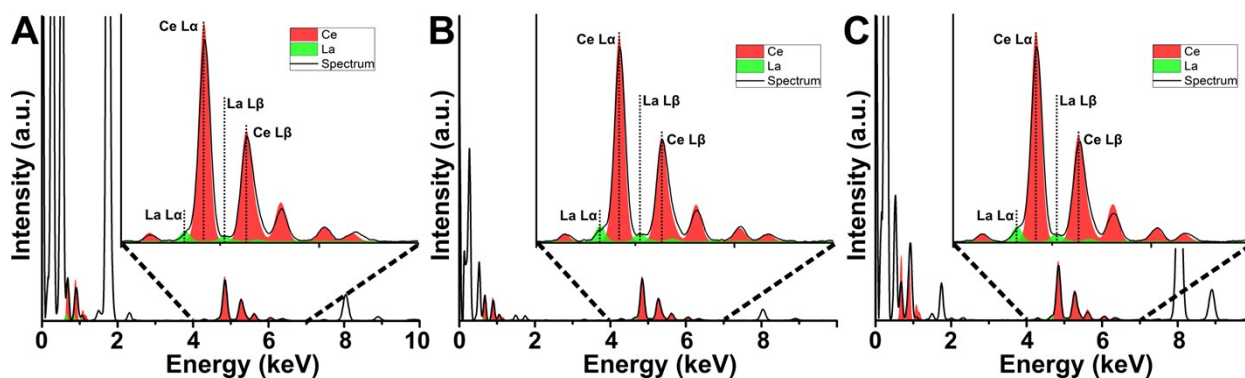


Fig. S3 AC-STEM-EDS full spectra and zoomed areas showing the $L\alpha$ peaks of Ce and La that were used for the quantification. The deconvoluted $L\alpha$ peaks of Ce and La are depicted in red and green, respectively. (A) Spectrum corresponding to the elemental maps of the nominal 5 mol% La-doped CeO_2 nanocubes presented in Figure 4D, E. (B) Spectrum corresponding to the elemental maps of the nominal 7.5 mol% La-doped CeO_2 nanocubes presented in Figure 5D, E. (C) Spectrum corresponding to the elemental maps of the nominal 10 mol% La-doped CeO_2 nanocubes presented in Figure 6D, E.

Figure S3A-C shows the AC-STEM-EDS spectra corresponding to the elemental maps presented in Figures 4-6. The quantification was performed using the L peaks of Ce ($L\alpha=4.839$ keV, $L\beta=5.261$ keV) and La ($L\alpha=4.650$ keV, $L\beta=5.041$ keV) and the resulting deconvoluted spectra are shown along with the EDS spectra in the zoomed areas of Figure S3A-C.

Further visible peaks can be identified as C ($K\alpha=0.277$ keV), O ($K\alpha=0.525$ keV), Si ($K\alpha=1.739$ keV, $K\beta=1.836$ keV) and Cu ($K\alpha=8.040$ keV, $K\beta=8.904$ keV) and are due to spurious contributions coming from the TEM grids and the detector.