Supplementary Information

Deciphering the Dual Reagent-Catalyst Behavior of Ceria Nanoparticles

Dmitry Galyamin, Lena M. Ernst, Aina Fitó-Parera, Guillem Mira-Vidal, Neus G. Bastús, Neus Sabaté and Victor Puntes

Zeta-potential of citrate-stabilized CeO2 NP suspension versus pH



Figure S1. Zeta-potential of citrate-stabilized CeO₂ NP suspension versus pH.

	λmax (nm)	$\epsilon (M^{-1} cm^{-1})$
ABTS	415	36.000 ¹
TMB	653	39.000 ²
DOPA	475	3.700^{3}
$[Fe(CN)_{6}]^{3-}$	420	1.040^{4}

 Table S1: Wavelength corresponding to the maximum absorbance and molar absorptivity of different molecules

X-ray Photoelectron Spectroscopy (XPS).

XPS analysis was employed to determine Ce^{3+}/Ce^{4+} species, recording the core level XPS spectra of Ce 3d. By following a peak-fitting procedure, Ce3d spectrum was analyzed using six peaks for Ce^{4+} (V, V", V"", U, U" and U"") (Fig. S2 in green), corresponding to three pairs of spin-orbit doublets, and four peaks (two doublets) for Ce^{3+} (V0, V', U0 and U') (Fig. S2 in blue), based on the peak positions reported by Mullins et al.⁵ where U and V refer to the 3d3/2 and 3d5/2 spinorbit components, respectively. Because of the highly nonstoichiometric nature of CeO2, both 3+ and 4+ states are present in CeO₂. Relative concentrations of cerium ions were calculated from the peak areas obtaining [Ce³⁺] of 36%.



Figure S2. Ce 3d XPS spectra of CeO₂ nanoparticles. Ce³⁺ peaks corresponding t0 v0, v', and u0 and u' are labelled in blue. Ce⁴⁺ peaks corresponding to v, v'' and v'', and u, u'' and u''' components are labelled in green. Experimental spectra black-dotted line. Fitted spectra red-solid line. Relative concentrations of cerium ions were calculated from the peak areas obtaining [Ce³⁺] of 36%.



Figure S3. Dissolution of CeO₂ Nanoparticles at Different pHs. CeO₂ NPs were exposed to different media at pH 4.4 and pH 1.7. A decrease of absorbance maximum with time confirms that NPs gradually dissolve. NPs dissolve faster at pH 1.7 than at pH 4.4. For pH 4.4, complete dissolution takes place after 62 hours, where the absorption profile coincides with that of CeCl₃ precursor at the concentration corresponding to that present in the volume of exposed NPs is used as a control (0.5 mM). The Initial drop (green square) corresponds to the first 3 hours of exposure, corresponding with ferrocyanide experiments. For pH 1.7, NPs completely dissolved after 3 hours.

Materials and methods

X-ray Photoelectron Spectroscopy (XPS) was performed on a SPECS system equipped with a monochromatic Al source operating at 300W and a Phoibos 150 analyzer. The pass energy of the hemispherical analyzer was set at 20 eV, and the energy step of high-resolution spectra was set at 0.05 eV. Binding energy (BE) values were referred to the C 1 s peak at 285.0 eV. Data processing was performed with the CasaXPS sofware. Cerium 3d spectra were analyzed using six peaks for Ce4+ (V, V", V", U, U" and U"'), corresponding to three pairs of spin-orbit doublets, and four peaks (two doublets) for Ce3+ (V0, V', U0 and U'), based on the peak positions reported by Mullins et al., where U and V refer to the 3d3/2 and 3d5/2 spin-orbit components, respectively. Samples were prepared by drop-casting the sample onto a clean silicon wafer.

Dissolution of CeO₂ Nanoparticles at different pHs. CeO₂ NPs (500 μ L, 1.72 mg/mL) were exposed to different media at pH 4.4 (citrate buffer, 9.5 mL, pH 4.4) and pH 1.7 (HCl, 2.85 mL, pH 1.7). Aliquots were extracted at different time points as labelled.

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