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Supplementary Information

New horizons in photocatalysis: the importance of mesopores for cerium oxide

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For the X-Ray Diffraction (XRD) measurements, the samples were initially sieved using a 48 μm size sieve. A X-ray diffractometer (Rigaku Ultima IV) working at the Bragg-Brentano geometry at 40 kV and 17 mA with a Cu Kα radiation source (1.5405 Å) was used. The measurements were performed in the 2θ range from 20° to 90° with a step size of 0.05° with an acquisition time of 4.5 s/point.

In order to determine the crystalline phases present in the diffractogram of each sample, the JCPDS-ICDD database was used. After this, the diffractograms were analyzed with the Fullprof Suite software version of july-2017 using the Rietveld refinement method.[1,2] The fluorite-type crystalline structure of CeO_2 and the atomic positions of Ce and O atoms at the base vectors were used as input in the Fullprof software. The number of cycles used in the refinement of each case was 30. Firstly, the diffractogram of a quartz standard sample was refined in order to obtain the equipment resolution file. Then, the diffractograms of the CeO_2 nanoparticles were refined. All refinements were performed using the following constraints:

- The V and W parameters of the reflection profile function were determined by refining the quartz standard sample and fixed to 0 for the analysis of the XRD patterns of the nanoparticles.

- The isotropic temperature parameter (B-factor) value of each atomic species was fixed to the value obtained in the crystallographic information file (CIF) of CeO_2.[3]
- The overall B-factor was allowed to have only positive values.
- The O occupancy number value was allowed to vary between the values that correspond to the completely oxidized cerium oxide (CeO_2) and the completely reduced cerium oxide (Ce_2O_3).
- The Ce occupancy number value was fixed to the value that corresponds to the completely oxidized cerium oxide (CeO_2)
- The correction for the 0 value in the 2θ scale was determined by refining the CeO_2 standard sample and then fixed to this value for all the CeO_2 nanoparticles.
- The transparency instrumental parameter was allowed to have only positive values.

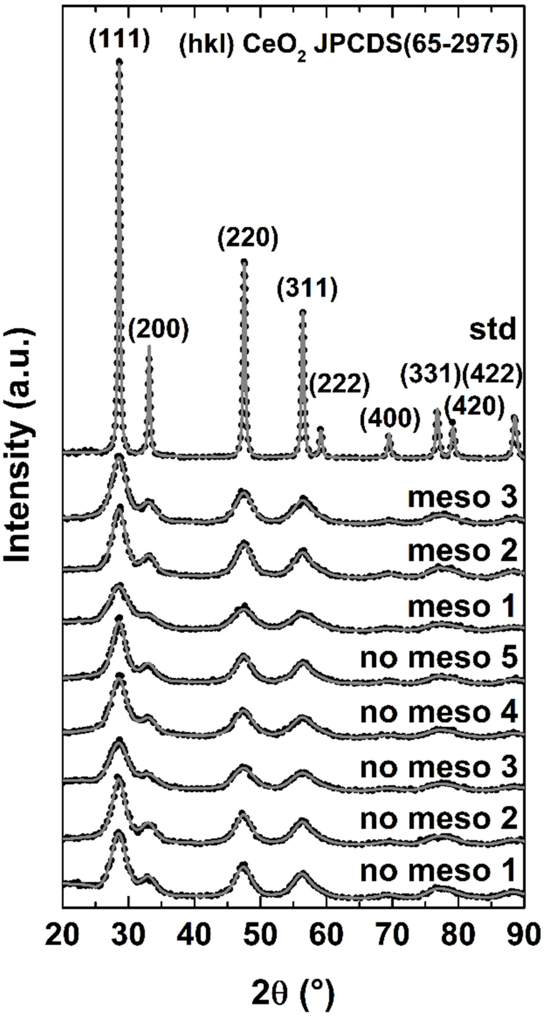

Figure S1 - Diffraction patterns of the cerium oxide nanoparticles and the result of Rietveld refinement. The points correspond to the experimental data. The gray solid line corresponds to the adjustment obtained by the Rietveld refinement.

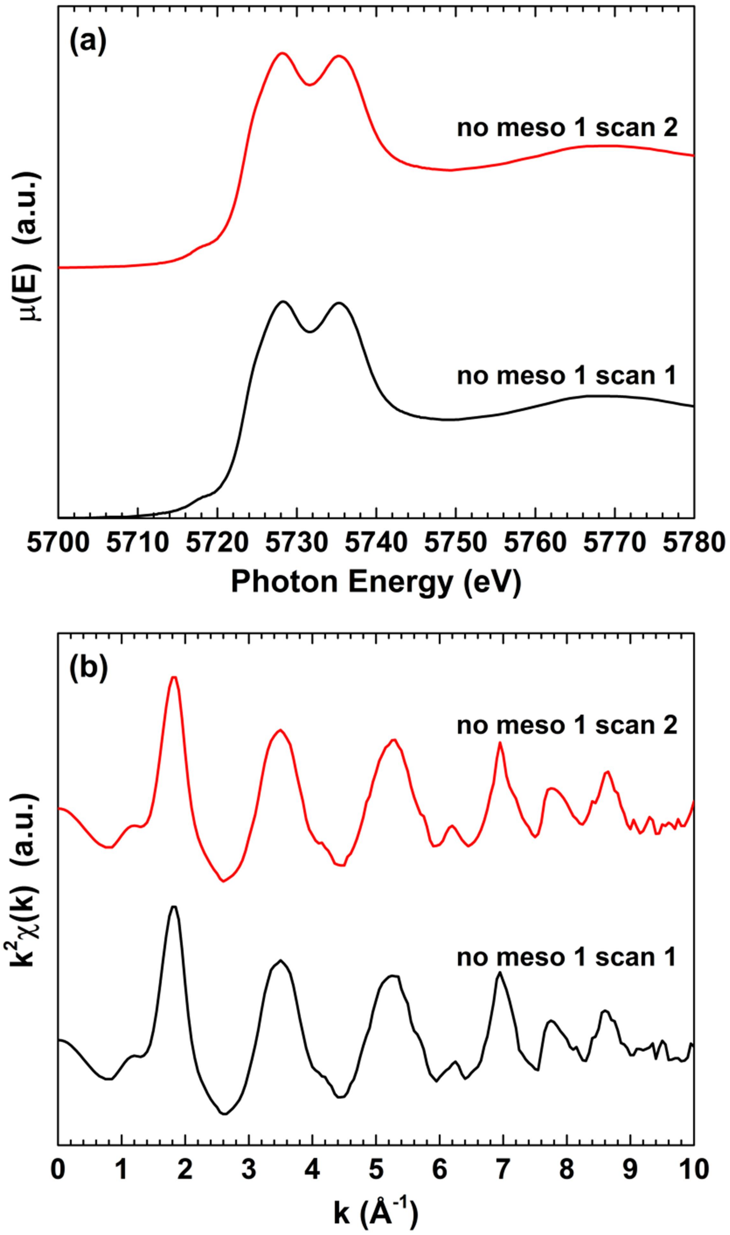

Figure S2 – Comparison between different scans of sample no meso 1 for the (a) XANES region and (b) EXAFS oscillations.

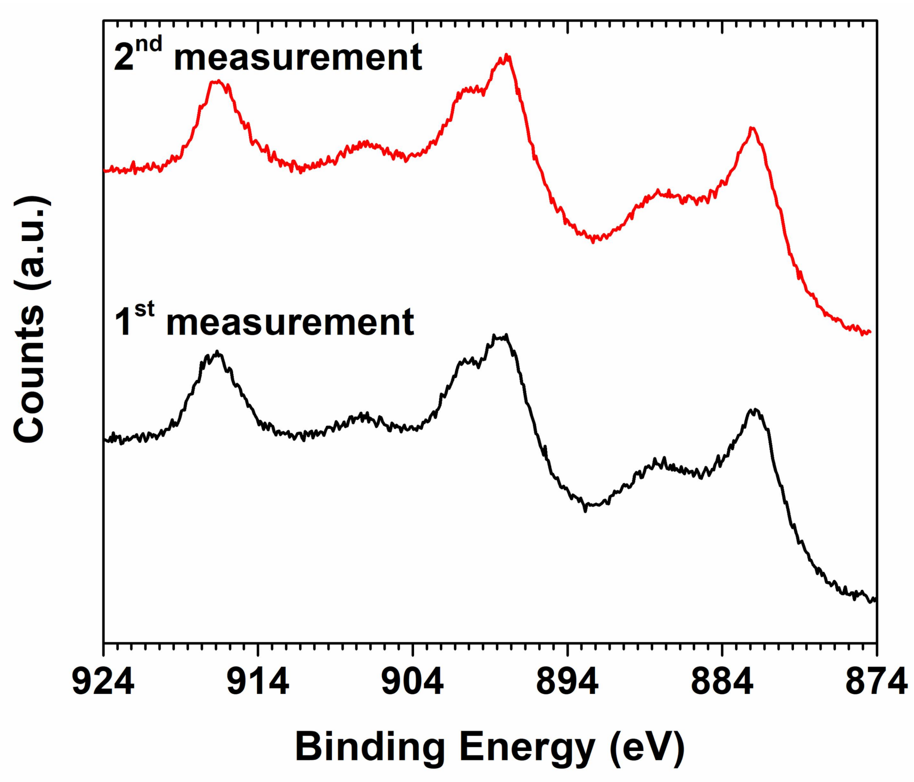

Figure S3 – Comparison between successive Ce 3d XPS spectra of meso 1 sample.

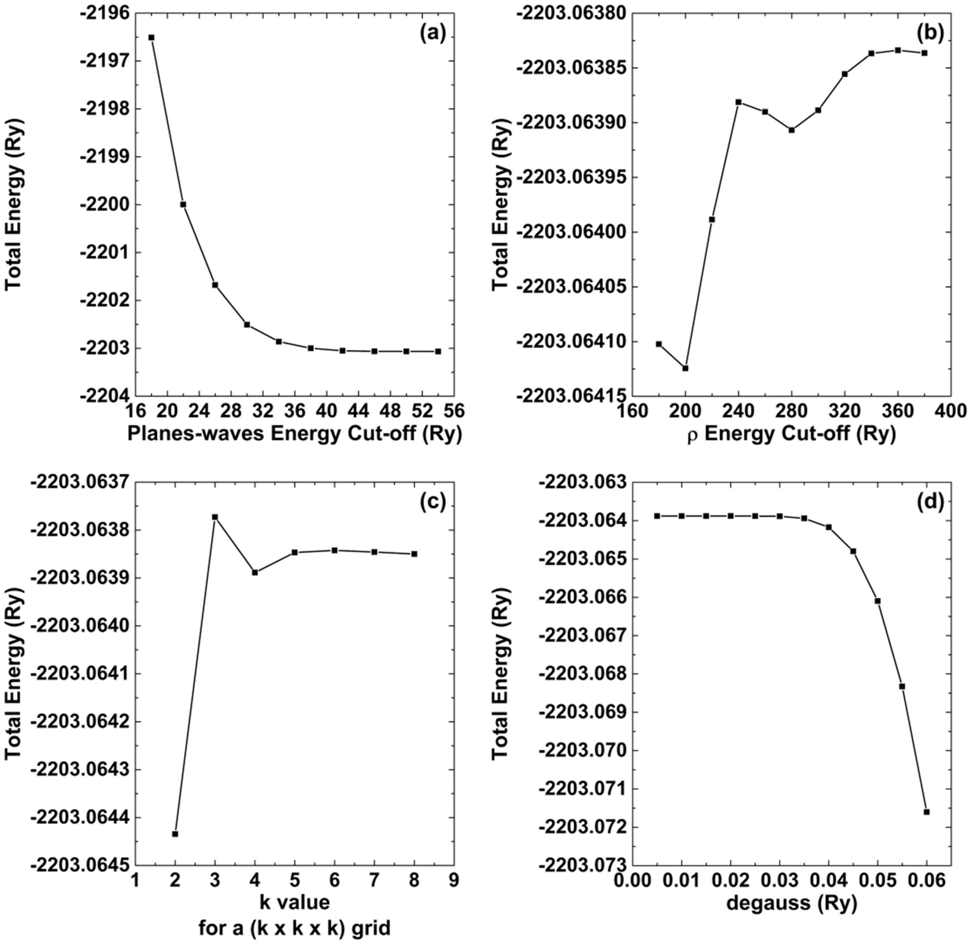

Figure S4 - Total energy obtained by the self-consistent calculations as a function of the (a) plane waves kinetic energy cut-off, (b) charge density (ρ) kinetic energy cut-off, (c) k-points grid size and (d) Gaussian smearing (degauss) parameter value.

In order to make sure that the structural properties of the cerium oxide are consistent with the information already known about this system, bulk DFT calculations of the cerium oxide with the presence of O vacancies were performed using 48 atoms (16 Ce atoms and 32 O atoms) in the fluorite-type crystalline structure of CeO_2 with zero, one and two O vacancies. The lattice parameters obtained from the relaxation calculations for the cases with zero, one and two O vacancies are 5.413 Å, 5.440 Å and 5.464 Å, respectively. The lattice parameter obtained from the calculation with zero O vacancies, 5.413 Å, is in great agreement with the experimental value from XRD measurements of the CeO_2 standard in the present work, differing by only 0.07%. Moreover, it is possible to observe that the lattice parameter value increases with the number of vacancies. This behaviour is well known for the cerium oxide and agrees with experimental results.[1,2] Moreover, the Kim's equation[1] allows obtaining the Ce(III) fraction using the lattice parameter of cerium oxide. In this case, Kim's equation relates the lattice parameters found in the DFT calculations for the cases with O vacancies to Ce(III) fractions of 0.117 and 0.221. These values are in accordance to the theoretical valaues of 0.125 (one O vacancy for 48 atoms of Ce + O) and 0.25 (two O vacancies for 48 atoms of Ce + O).

For the Fourier Transform Infrared Spectroscopy (FTIR) measurements, about 0.1 mg of the nanoparticle powder was mixed with 100 mg of KBr powder, and this mixture was compacted to produce homogeneous pellets. The measurements were performed at room temperature using a FTIR spectrophotometer (Shimadzu IRPrestige-21) in transmittance mode to obtain the FTIR spectra in the wavelength range from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 2 cm^{-1}.

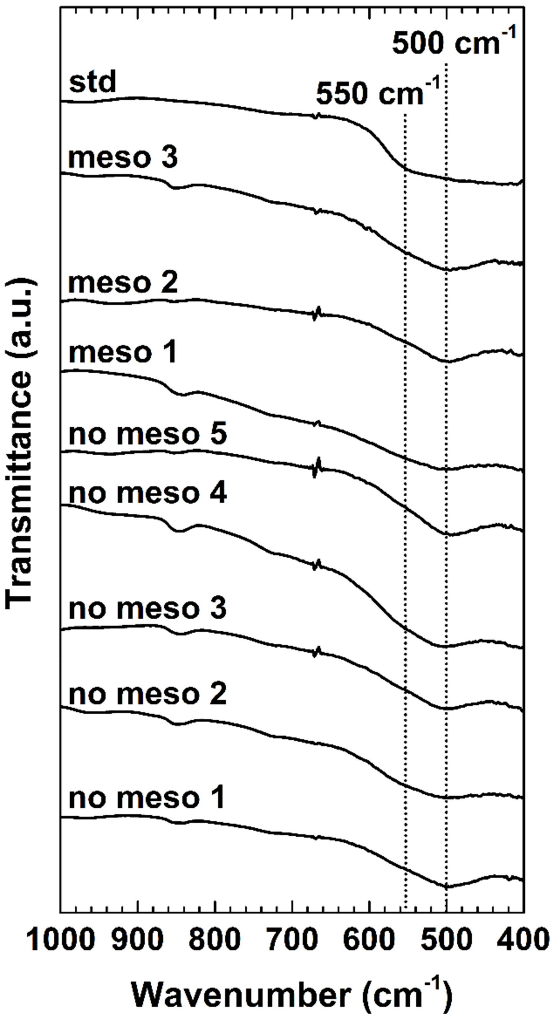

Figure S5 - FTIR spectra of the cerium oxide nanoparticles from 400 cm^{-1} to 1000 cm^{-1}. The dotted lines indicate the absorption bands associated to the Ce-O stretching vibration present at 550 cm^{-1} for the standard sample and around 500 cm^{-1} for the other nanoparticles.

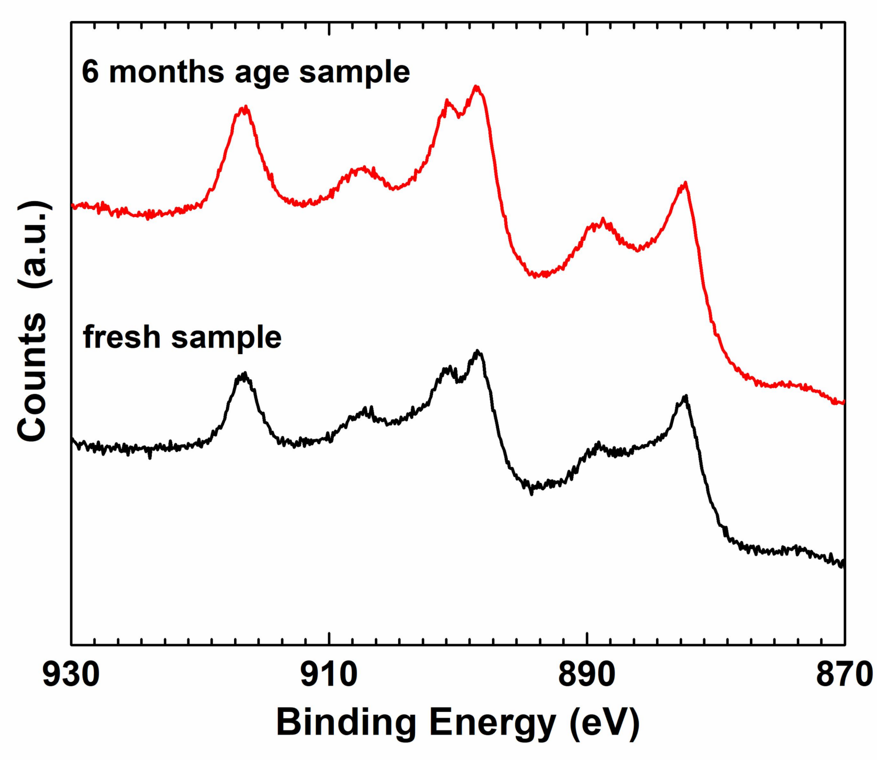

Figure S6 – Comparison between the Ce 3d XPS spectrum of meso 2 sample fresh and with 6 months age.

Table S1 – Band gap energy, H_2 evolution photocatalytic activity and H_2 evolution photocatalytic activity normalized by the surface area of the cerium oxide nanoparticles. The uncertainty on the band gap values is around 0.03 eV in all cases.

Sample	E_g (eV)	H_2 evolution photocatalytic activity (μmol h^{-1} g^{-1})	H_2 evolution photocatalytic activity / surface area (μmol m^{-2} h^{-1})
no meso 1	2.88	76 ± 5	0.55 ± 0.04
no meso 2	2.97	55 ± 4	0.42 ± 0.04
no meso 3	2.88	74 ± 6	0.71 ± 0.07
no meso 4	2.96	81 ± 6	0.64 ± 0.05
no meso 5	3.00	68 ± 3	0.41 ± 0.02
meso 1	2.79	25 ± 1	0.18 ± 0.01
meso 2	2.73	112 ± 5	0.66 ± 0.04
meso 3	3.00	7 ± 1	0.035 ± 0.005
standard	3.16	11 ± 1	0.29 ± 0.05

Table S2 - Ξ^{XANES} values of the cerium oxide nanoparticles obtained by the fitting performed in the XANES region of the X-ray absorption spectra, and the parameters obtained from the fitting of the EXAFS region. The uncertainty associated to the Ξ^{XANES} values is around 0.05. For the Ce-H scattering path, the uncertainties obtained in the fit procedure for the R and σ^2 values are around 0.01 Å and 0.7 x 10^{-3} Å^{-1}, respectively. For the Ce-O scattering path, the uncertainties obtained in the fit procedure for the R and σ^2 values are around 0.002 Å and 0.3 x 10^{-3} Å^{-2}, respectively. The Ce-O distance calculated from the Rietveld refinement results is shown as well.

Sample	Ξ^{XANES}	Ce-H Scattering Path		Ce-O Scattering Path			R_{Ce-O}^{XRD} (Å)
		N	R (Å)	N	R (Å)	σ^2 (10^{-3} Å^{-2})	
no meso 1	0.09	4 ± 1	1.65	7.64	2.304	9.3	2.348
no meso 2	0.05	4 ± 1	1.66	7.79	2.323	8.5	2.347
no meso 3	0.09	4 ± 1	1.67	7.64	2.320	9.4	2.347
no meso 4	0.06	4 ± 1	1.66	7.76	2.321	8.9	2.347
no meso 5	0.06	4.4 ± 0.9	1.64	7.76	2.333	9.8	2.345
meso 1	0.11	2.9 ± 0.8	1.70	7.57	2.313	10.2	2.347
meso 2	0.12	3.5 ± 0.6	1.71	7.52	2.306	10.2	2.345
meso 3	0.06	4.0 ± 0.9	1.64	7.75	2.326	8.3	2.345
standard	0.00	0.00	-	8.00	2.317	4.1	2.342

References

[1] M. Mogensen, N. M. Sammes, G. A. Tompsett, *Solid State Ionics* **2000**, *129*, 63–94.

[2] A. Kossoy, A. I. Frenkel, Y. Feldman, E. Wachtel, A. Milner, I. Lubomirsky, *Solid State Ionics* **2010**, *181*, 1473–1477.