Electronic Supplementary Information

Synthesis routes of CeO_2 nanoparticles dedicated to organophosphorus degradation : a benchmark

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1) Production yield of the Photochemical (Xhv) method

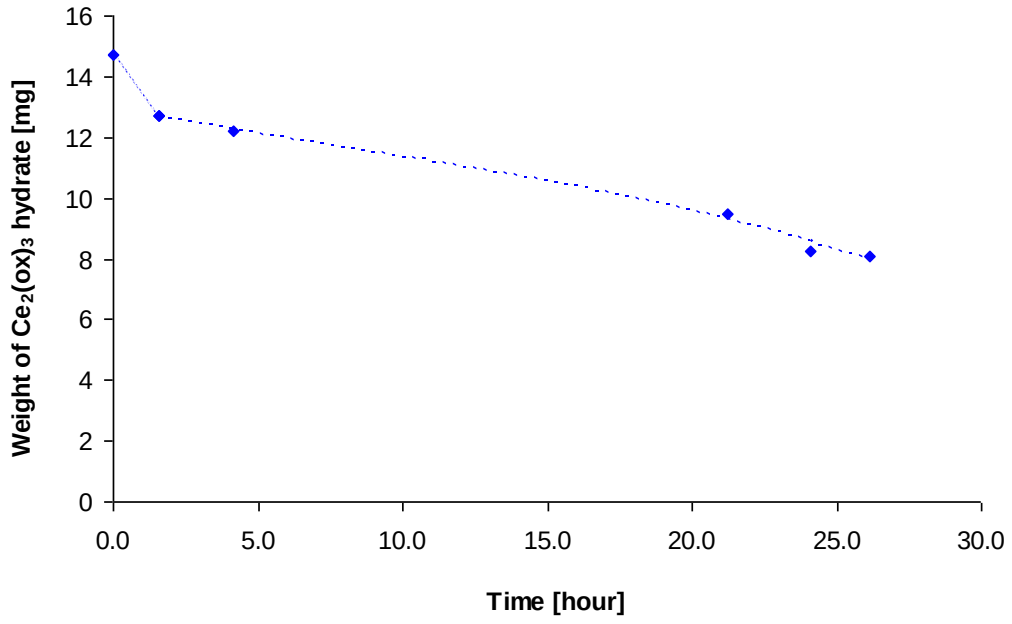

Figure S1: Weight of cerium oxalate hydrate measured in 8 mL samples from the large-scale synthesis as a function of the reaction time. The cerium oxalate hydrate corresponds to the unreacted Ce^{3+} ions.

Figure S1 shows the evolution of the weight of cerium oxalate hydrate measured in 8 mL samples from the large-scale synthesis as a function of the reaction time. The cerium oxalate hydrate is formed from the unreacted Ce^{3+} ions. The Ce^{3+} concentration decreases very slowly. The slow kinetics is probably due to the absorption of the UV light by the formed particles which lowers the amount of light available for the photochemical reactions. From the time evolution of the cerium oxalate hydrate weight displayed in Figure S1, we can deduce that the preparation yield of CeO_2 is 38% after 26 hours (the ratio between the final and the initial weight of cerium oxalate hydrate is 62%).

2) <u>Volume weighted size distribution of the Φ-NPO sample</u>

The particle size distribution is measured with a Mastersizer 3000 from Malvern based on the technique of laser diffraction. A droplet of the pristine solution is injected in the flow system and the Mie scattering

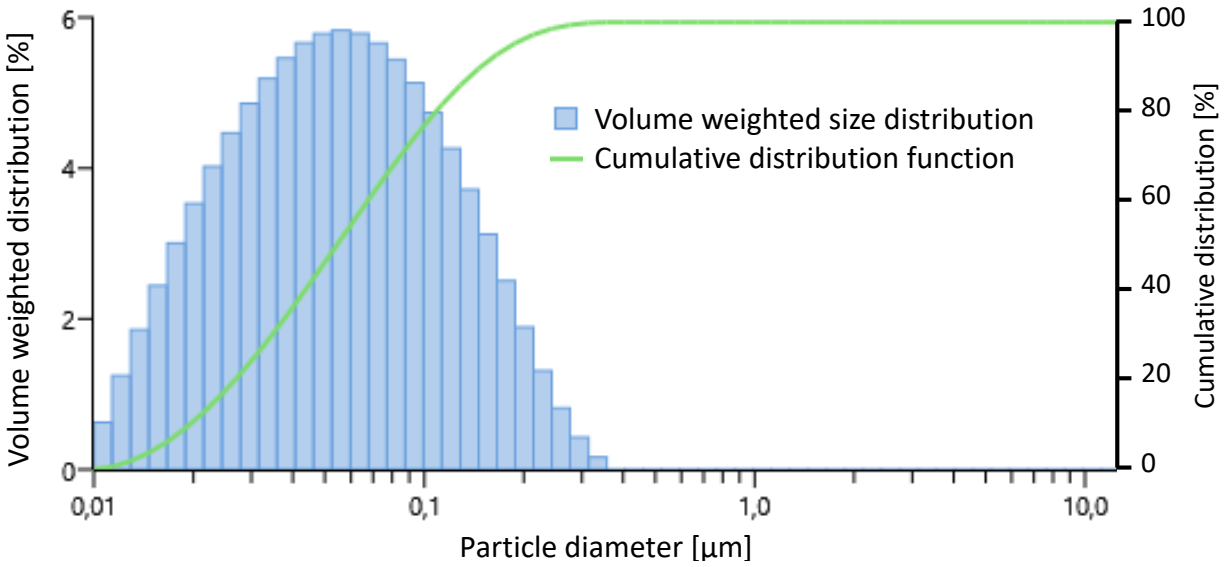

Figure S2: Volume weighted size distribution of the Φ-NPO sample and the corresponding cumulative distribution function

model was used. Figure S2 shows the volume weighted size distribution delivered by the Mastersizer 3000 particle size analyzer, as well as the cumulative distribution function. 10% (volume percent) of the particles have a diameter below 19.5 nm, 50% below 54.7 nm, and 90% below 154 nm. The distribution is consistent with the sizes observed on the HRTEM images (Figure 2A) from a few nanometers to a few hundred nanometers.

3) TEM and HRTEM images of the CeO_2 nanoparticles after annealing

Figure S3 shows TEM and HRTEM images of the samples annealed in air at 500°C for two hours.

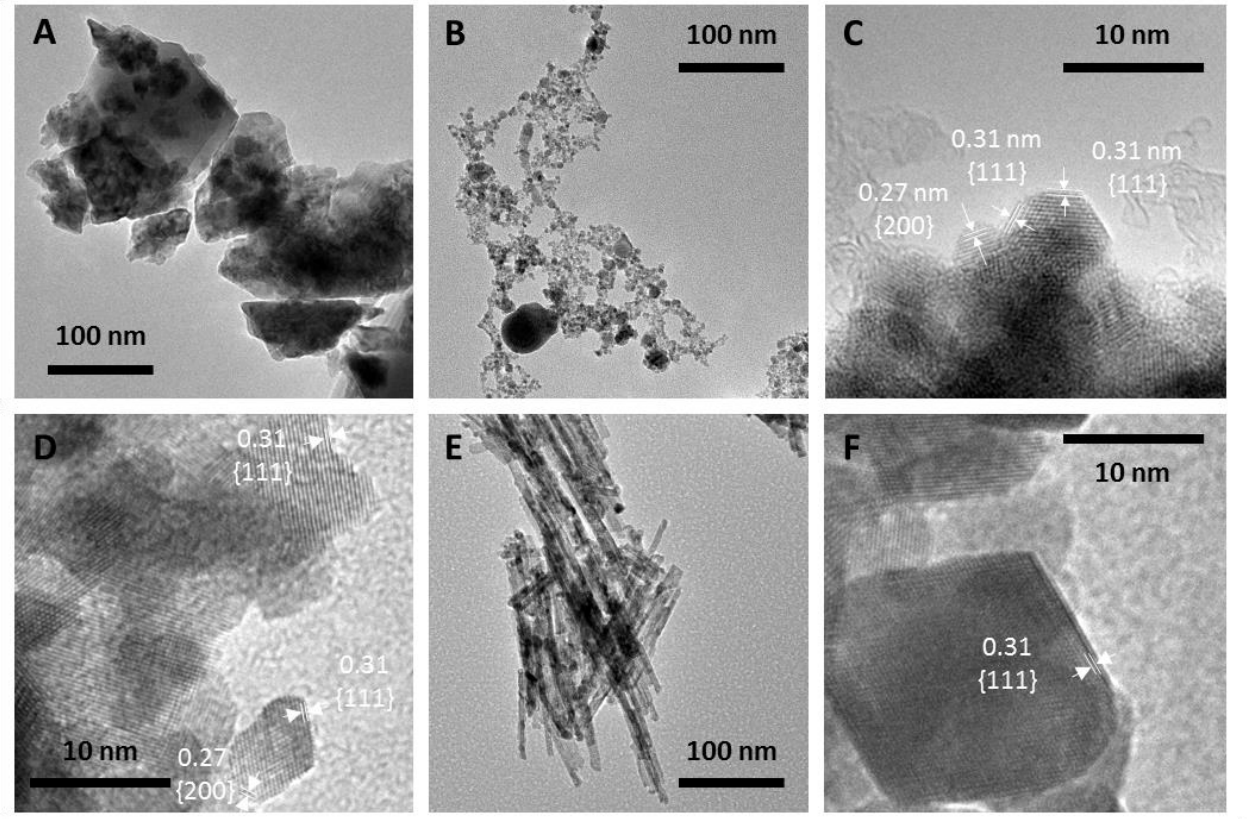

Figure S3: Bright field TEM and HRTEM images of the samples after the annealing treatment. (A) Commercial nanopolyedra Φ-NPO*. (B,C) Nanotruncated octahedra synthesized by PLAL Φ-NTO*. (D) Nanotruncated octahedra elaborated by photochemistry Xhv-NTO*. (E) nanorods X-NR* and (F) nano-octahedra X-NO* elaborated by hydrothermal process.

4) Raman spectra

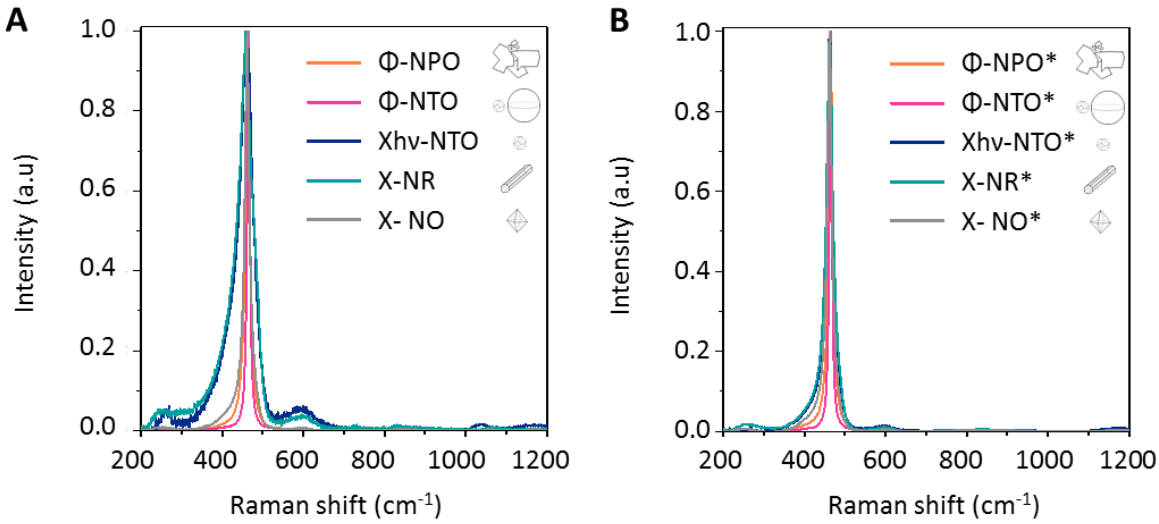

Figure S4: Raman spectra of the cerium oxide nanoparticles before (A) and after (B) the annealing treatment in the 200-1200 cm^{-1} range (λ_{exc} = 633 nm). All spectra are normalized relative to the maximum intensity of the F_{2g} mode of the CeO_2 fluorite phase.

5) Infrared spectroscopy

Species	Peak wavenumber (cm^{-1})					Vibration mode
	Φ-NPO	Φ-NTO	Xhν-NTO	X-NR	X-NO	
adsorbed water or –OH group	~ 3400		~3200	~ 3400	~ 3400	ν(OH)
Formate or ligand	2959(sh), 2922, 2857, 2849(sh)		2842			ν(CH)
adsorbed water or –OH group	1630		1630(sh)	1639	1631	δ(OH)
Carboxylate ions R-CO_2^- (formate or ligand)	1538, 1457, 1406, 1337(sh)		1553, 1467 (sh), 1377(sh), 1352			νas(OCO) and νs(OCO)
Carbonate				1540, 1330	1540, 1330	ν(CO)
Hydrogen carbonate HO-COO^-		1262				δ(COH)
Hydrogen carbonate HO-COO^-		1100				ν(CO)
carbonate	1068	1020(sh)	1058	1050	1050	ν(CO)
carbonate	842(sh), 712	802, 715	833, 753	847, 715(sh), 667	850, 714(sh), 666	δout(CO_3) and δin(CO_3)
cerium oxide	< 600	< 600	< 600	< 600	< 600	ν(Ce-O)

Table S1 – Assignment of absorbance peaks observed in FTIR spectra for the as-produced samples, before annealing. Symbol ν and δ represent the stretching vibration and the bending vibration respectively. δout names a bending out-of-plan, δin a bending in-plane, νas an asymmetric stretching, and νs a symmetric bending. The annotation (sh) means that the corresponding vibration mode is marked by a shoulder.

6) Costs

The Excel file costs.xlsx gathers all the information regarding the cost assessments as well as the productivity.