Electronic Supplementary Information

Single-phase ZrO_2 nanocrystals obtained by solvothermal synthesis with different growth controlling-agents

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Table S1. Raman shift values observed for ZrO_2 samples synthesized in different solvents and different zirconium butoxide concentration.

Raman shift (cm^{-1})		
$[Zr(OBut)_4]$ = 0.25 M		
Solvent		
oleic acid	**benzyl alcohol**	**octyl alcohol**
179	141	146
217	255	179
306	307	217
330	451	269
344	633	316
381		330
478		381
501		474
538		501
556		538
615		556
		615
		638
$[Zr(OBut)_4]$ = 0.5 M		
Solvent		
oleic acid	**benzyl alcohol**	**octyl alcohol**
179	269	146
269	311	269
307	460	311
330	637	460
380		602
478		642
556		
611		

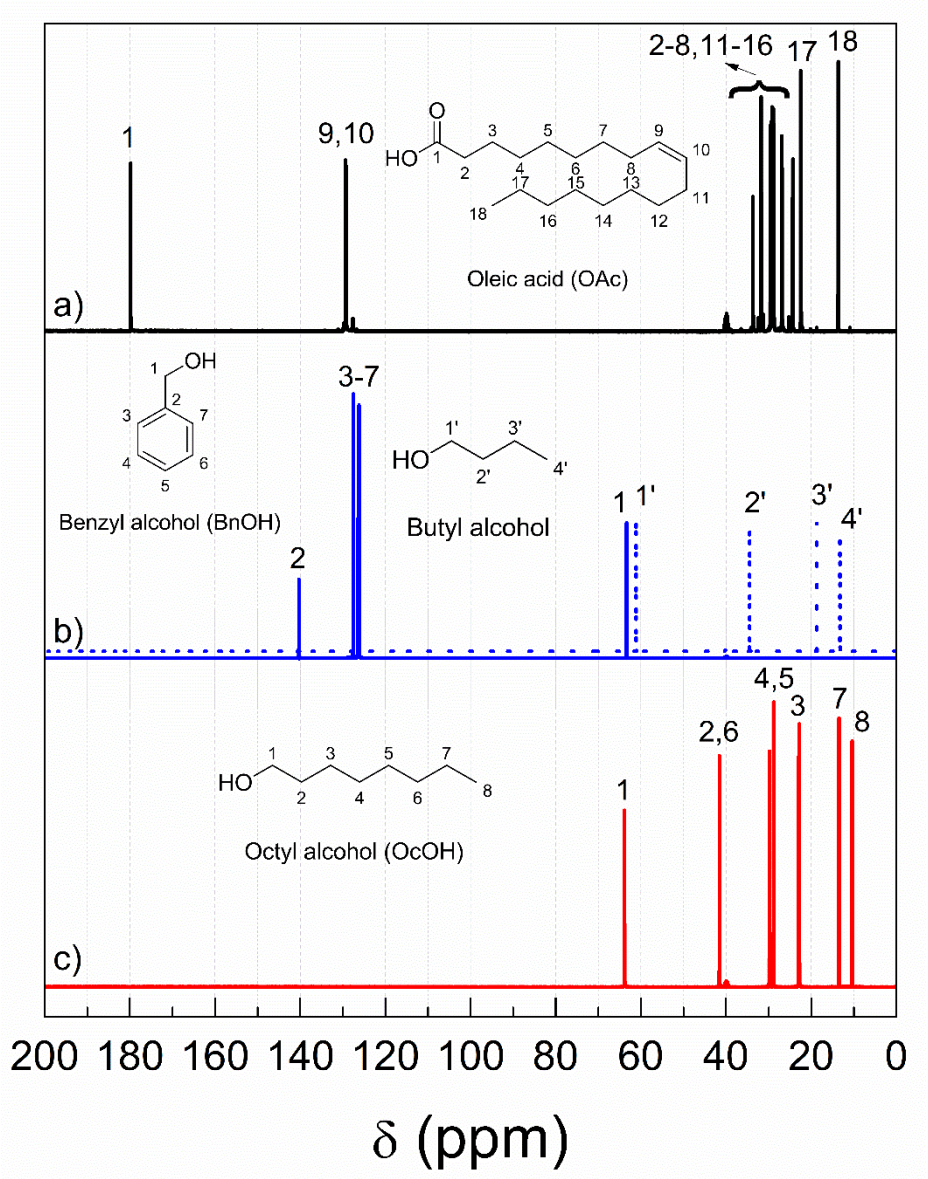

Figure S1. Solution ^{13}C NMR spectra of the solvents used in the reaction systems: (a) oleic acid; (b) benzyl alcohol (solid line) and butyl alcohol (dashed line); (c) octyl alcohol.

Table S2. Spectral assignments of the signals detected in the solution ^{13}C NMR spectra obtained for the solvents used in the syntheses.

Oleic acid		Benzyl alcohol		Butyl alcohol		Octyl Alcohol	
δ (ppm)	**Carbon**	**δ (ppm)**	**Carbon**	**δ (ppm)**	**Carbon**	**δ (ppm)**	**Carbon**
13.64	C18	63.34	C1	13.25	C4’	10.40	C8
22.45	C17	125 – 129	C3-7	18.71	C3’	13.48	C7
24 – 35	C3	140.28	C2	34.47	C2’	22.77	C6
28.7	C2-8, C11-16			161.13	C1’	28.83	C5
129.35	C9, C10					29.81	C4
179.8	C1					41.53	C2, C3
						63.82	C1

Table S3. Spectral assignments of the signals detected in the ^{13}C CP/MAS NMR spectra obtained for the ZrO_2 NCs.

ZrO_2 – OAc		ZrO_2 – BnOH		ZrO_2 – OcOH	
δ (ppm)	**Carbon**	**δ (ppm)**	**Carbon**	**δ (ppm)**	**Carbon**
14.79	C18	118.28 – 144.18	C2-C7	17.08	C8
17.34 – 49.18	C2-8, C11-17	173.48	dC	23.44	C7
131.14	C9, C10	13.40	C4’	27.27	C3
28.7	C8, C11	18.92	C3’	34.06	C4, C5
182.63	C1	38.88	C2’	43.83	C6
		183.25	dC’	53.59	C2
				187.35	dC

Determination of number of ligand molecules per surface area on the nanocrystals

From the TGA curves (Figure 8), the DTG curves (Figure S2) were obtained, in order to evidence the mass losses. A mass loss was observed around 330 °C for the samples synthesized in benzyl alcohol and octyl alcohol, being associated to a butanoate type of ligand. The curves shown in Figure S2b and c were deconvoluted into two Gaussian components (Figure S3). The area of the Gaussian peak centered at 330 °C was taken as

the butanoate content and normalized with respect to the total organic mass loss (associated with the total area of the fitted DTG curves).

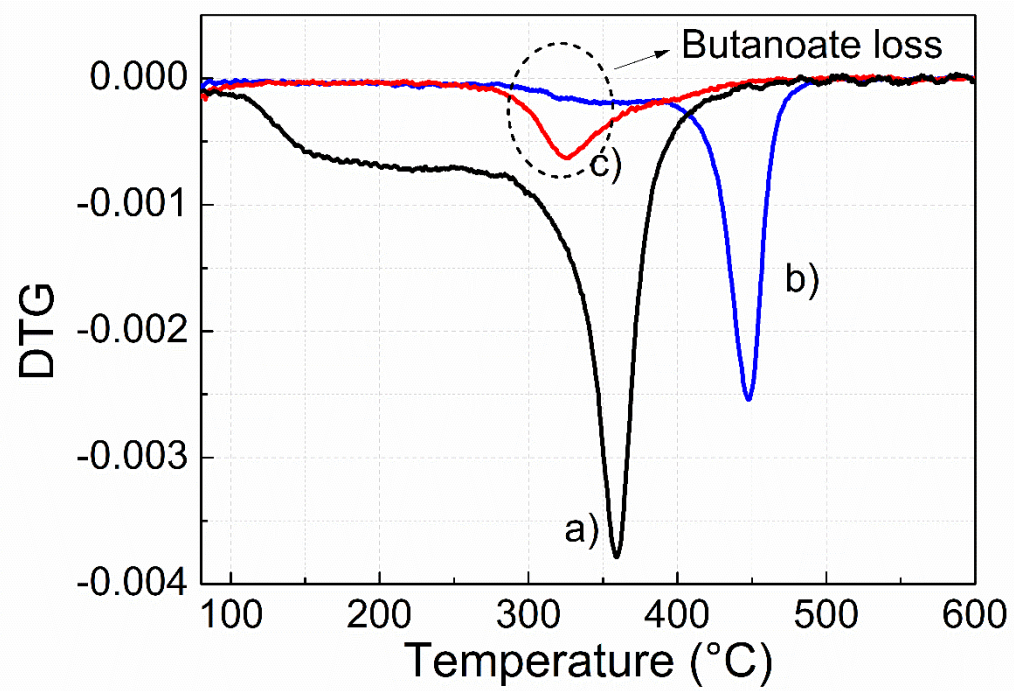

Figure S2. DTG curves obtained for the ZrO_2 NCs synthesized in (a) oleic acid, (b) benzyl alcohol and (c) octyl alcohol.

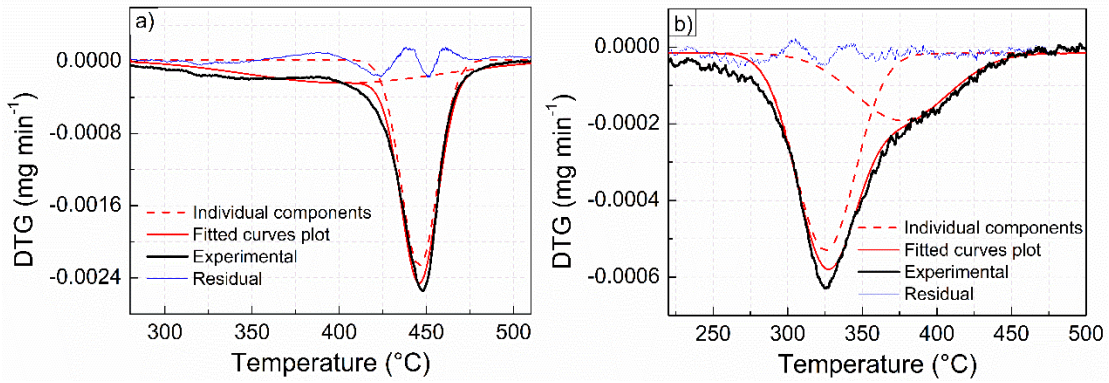

Figure S3. Deconvolution of DTG curves obtained for the ZrO_2 NCs synthesized in (a) benzyl alcohol and (b) octyl alcohol.

With the DTG analysis, it was then possible to determine the mass contents of organic ligands from the TGA curves, as 36.4% (oleate); 12.6% (4.6% butanate and 8.0% benzoate) and 6.5% (4.2% butanoate and 2.3% octanoate) for the samples synthesized in

OAc, BnOH and OcOH, respectively. These results were correlated with the molecular mass of each organic ligand, giving the result in equation S1. The specific surface area was estimated from the average particle sizes obtained from the analysis of the TEM images, using either equation S2 (assuming nearly spherical particles for the samples synthesized in benzyl alcohol) or equation S3 (assuming cylindrical particles for the samples synthesized in oleic acid and octyl alcohol). Finally, combining equation S1 and equations S2 and S3, the number of ligand molecules per area unit on the surface of the nanocrystals can be estimated (equation S4).

$$\frac{N}{m_{ZrO_2}} = \frac{\left(\%m_{lig}/\%m_{ZrO_2}\right)}{MM_{lig}} \cdot N_A \quad , \tag{S1}$$

where:

N = number of ligand molecules;

m_{ZrO2} = mass of zirconia;

$\%m_{lig}$ = ligand mass content on the sample obtained by TGA experiments;

$\%m_{ZrO2}$ = zirconia mass content on the sample obtained by TGA experiments;

MM_{lig} = ligand molar mass;

N_A = Avogadro number.

$$\frac{A_S}{m_{ZrO_2}} = \frac{4\pi r^2}{V_{ZrO_2} \cdot \rho_{ZrO_2}} = \frac{4\pi r^2}{(4/3)\pi r^3 \cdot \rho_{ZrO_2}} = \frac{3}{r \cdot \rho_{ZrO_2}} \quad , \tag{S2}$$

$$\frac{A_S}{m_{ZrO_2}} = \frac{2\pi r(r+h)}{V_{ZrO_2} \cdot \rho_{ZrO_2}} = \frac{2\pi r(r+h)}{\pi r^2 h \cdot \rho_{ZrO_2}} = \frac{2(r+h)}{rh \cdot \rho_{ZrO_2}} \quad , \tag{S3}$$

where:

A_S = surface area;

V = volume of the particles;

r = average particle width obtained from TEM results;

h = average particle length obtained from TEM results;

$\%m_{lig}$ = ligand mass content on the sample obtained by TGA experiments;

ρ_{ZrO2} = zirconia specific mass.

Taking the ratio from the results of equation S1 and S2 or S3:

$$\frac{N/m_{ZrO_2}}{A_S/m_{ZrO_2}} = \frac{N}{A_S} \tag{S4}$$