Supplementary materials for

Function of various levels of hierarchical organization of the porous $Ce_{0.9}REE_{0.1}O_{1.95}$ mixed oxides in the catalytic activity.

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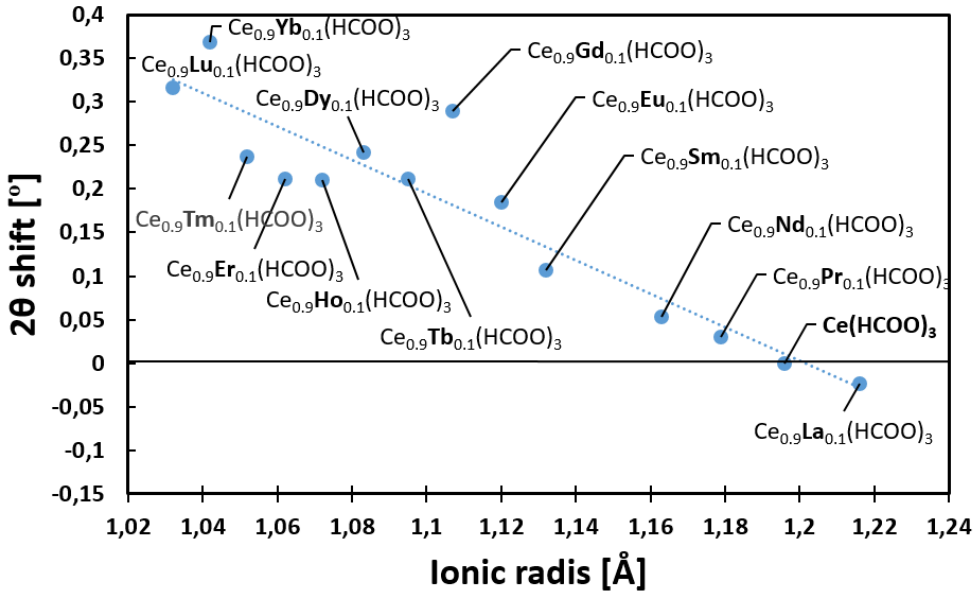


Fig. S1. 2θ angle shift of (411) peak in $Ce_{0.9}Ln_{0.1}(HCOO)_3$ samples (indicator of latticeconstant change) as a function ionic radius (Ln refers to lanthanide ion).

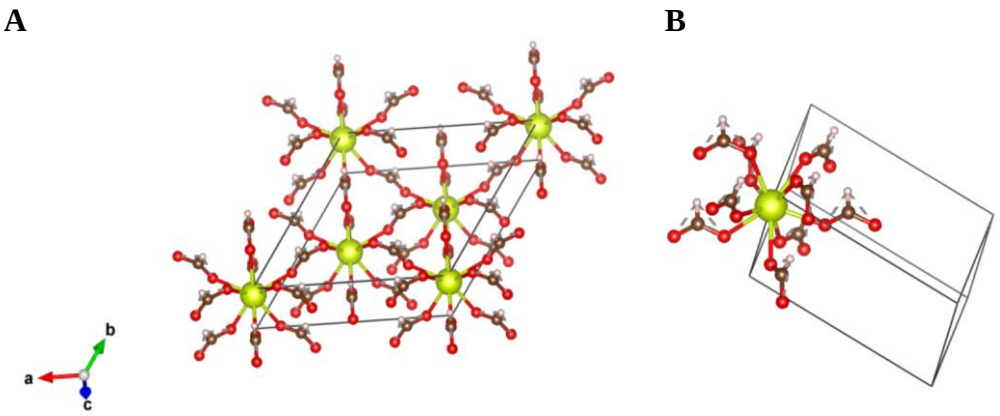


Fig S2. A. Crystal structure of $Ce(HCOO)_3$ (ref. ICSD: 237331); colour codes: cerium (yellow), oxygen (red), carbon (brown), hydrogen (white); B. Ce^{3+}(IX) surrounded by nine $HCOO_3$ molecules.

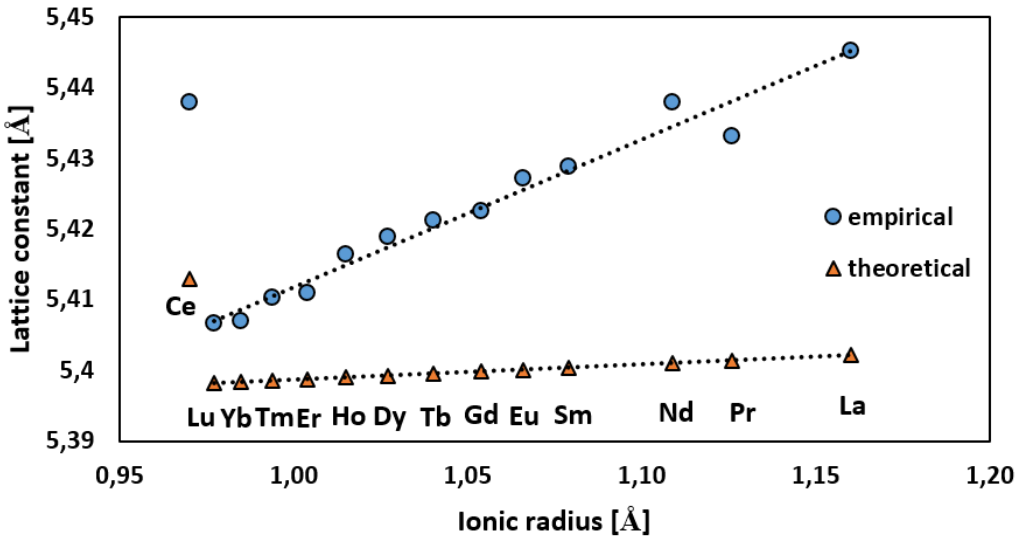


Fig. S3. Lattice constant as a function of ionic radius; Blue circles: Empirical data obtained from Rietveld refinement analysis of PXRD data of star-shaped particles; orange triangles: Lattice constant calculated from Kim's formula for doped cerium oxides [ref. D.-J. Kim, J. Am. Ceram. Soc. 72 (1989) 1415.]

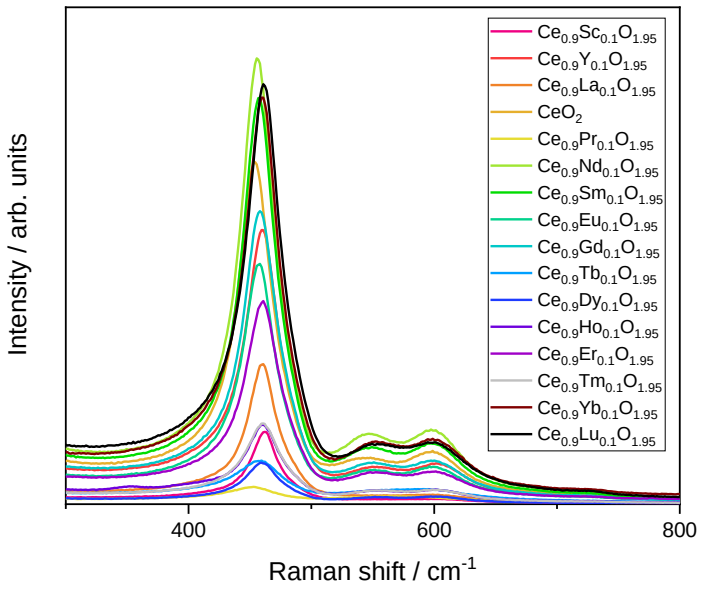


Fig. S4. Raman spectra of star-shaped $Ce_{0.9}RE_{0.1}O_{1.95}$ samples.

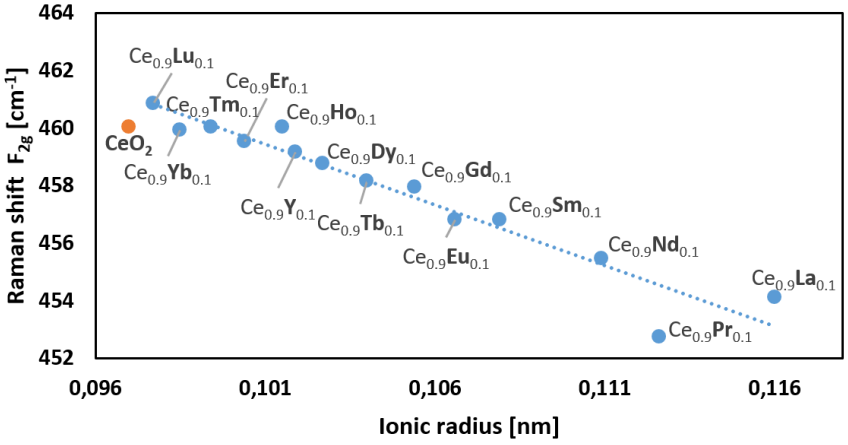


Fig S5. Raman F_{2g} mode shift for lanthanide series
Shift of CeO_2 F_{2g} mode from theoretical value of 465 cm^{-1} to 460 cm^{-1} may be due to crystal size decrease as suggested in [Spanier JE, Robinson RD, Zhang F, Chan SW, Herman IP (2001) Phys Rev B 64:245407].

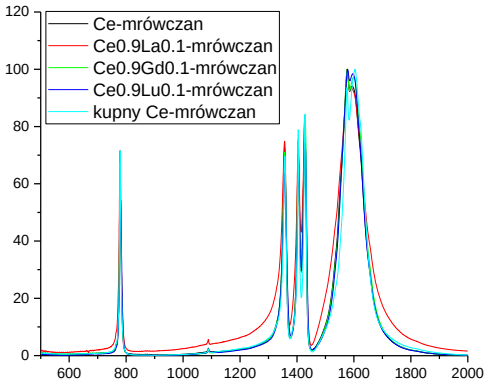


Fig. S6 IR spectra of $Ce_xRE_{1-x}(HCOO)_3$ samples (x= 0; 0.1; RE- La, Gd, Lu)

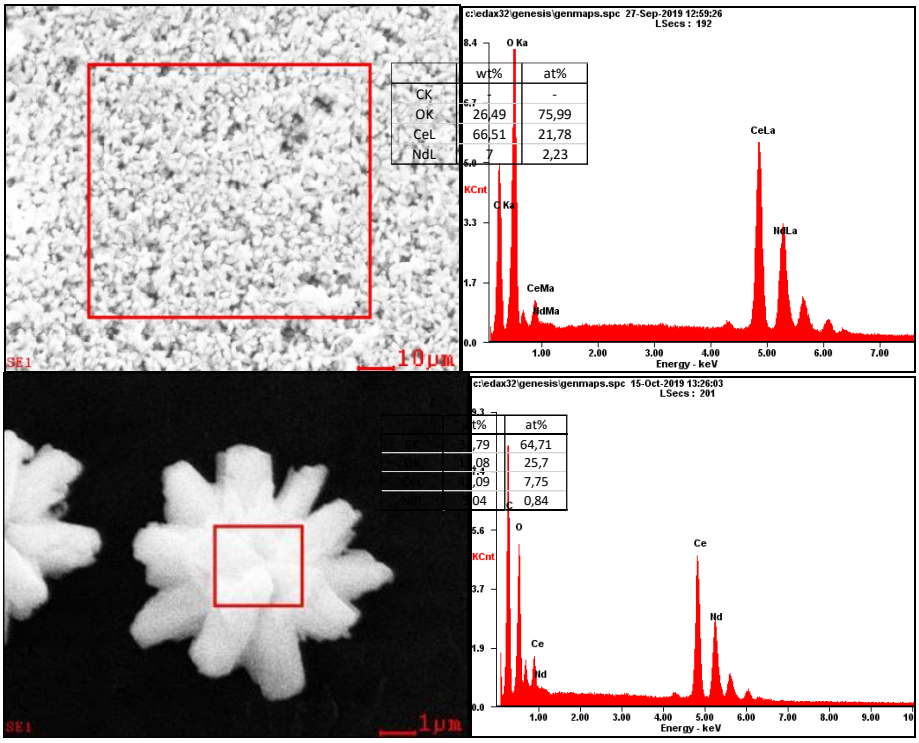


Fig. S7. EDS measurements of $Ce_{0.9}Nd_{0.1}(HCOO)_3$ sample as a presentation of the way of composition determination; A) Global composition; B) local composition.

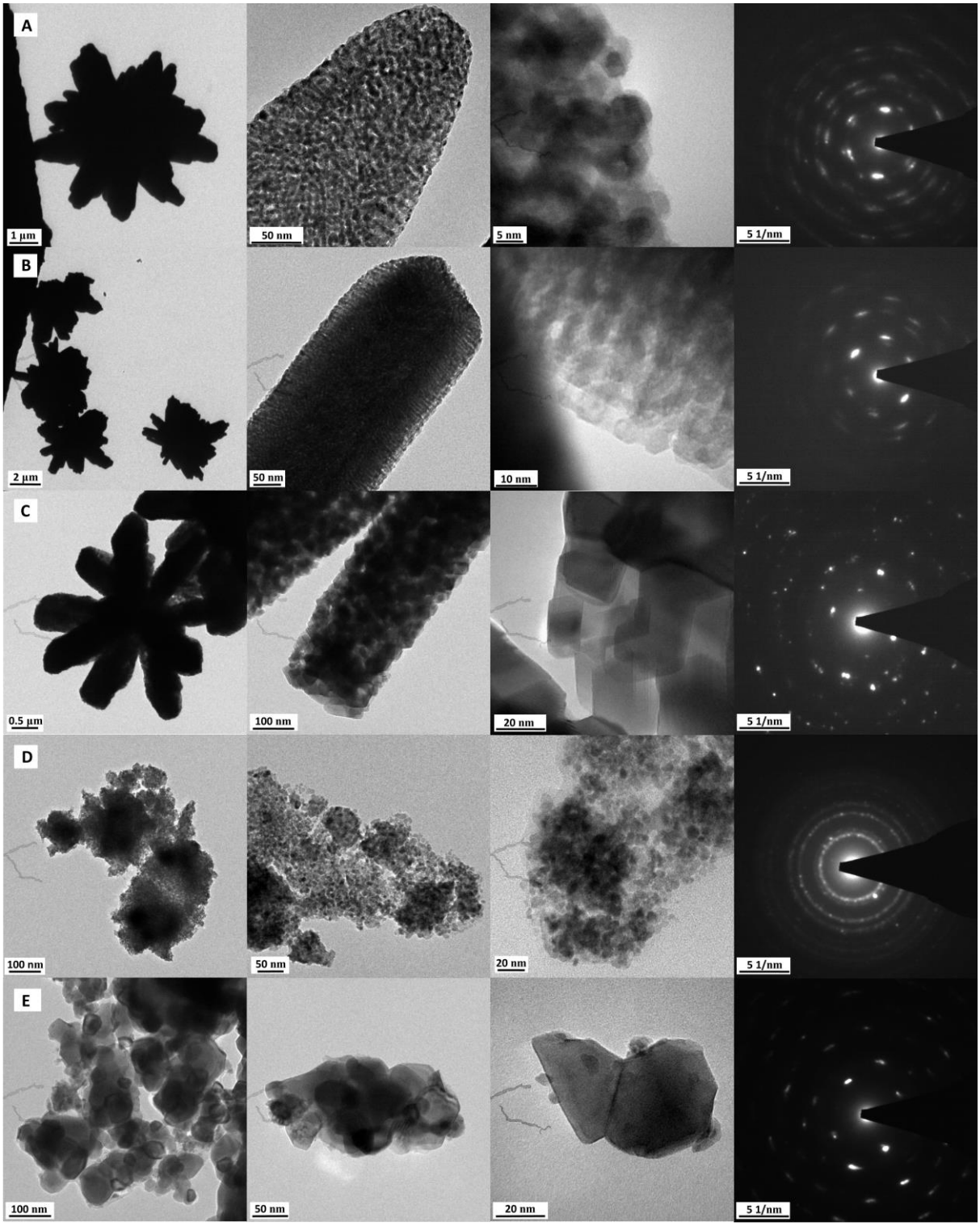
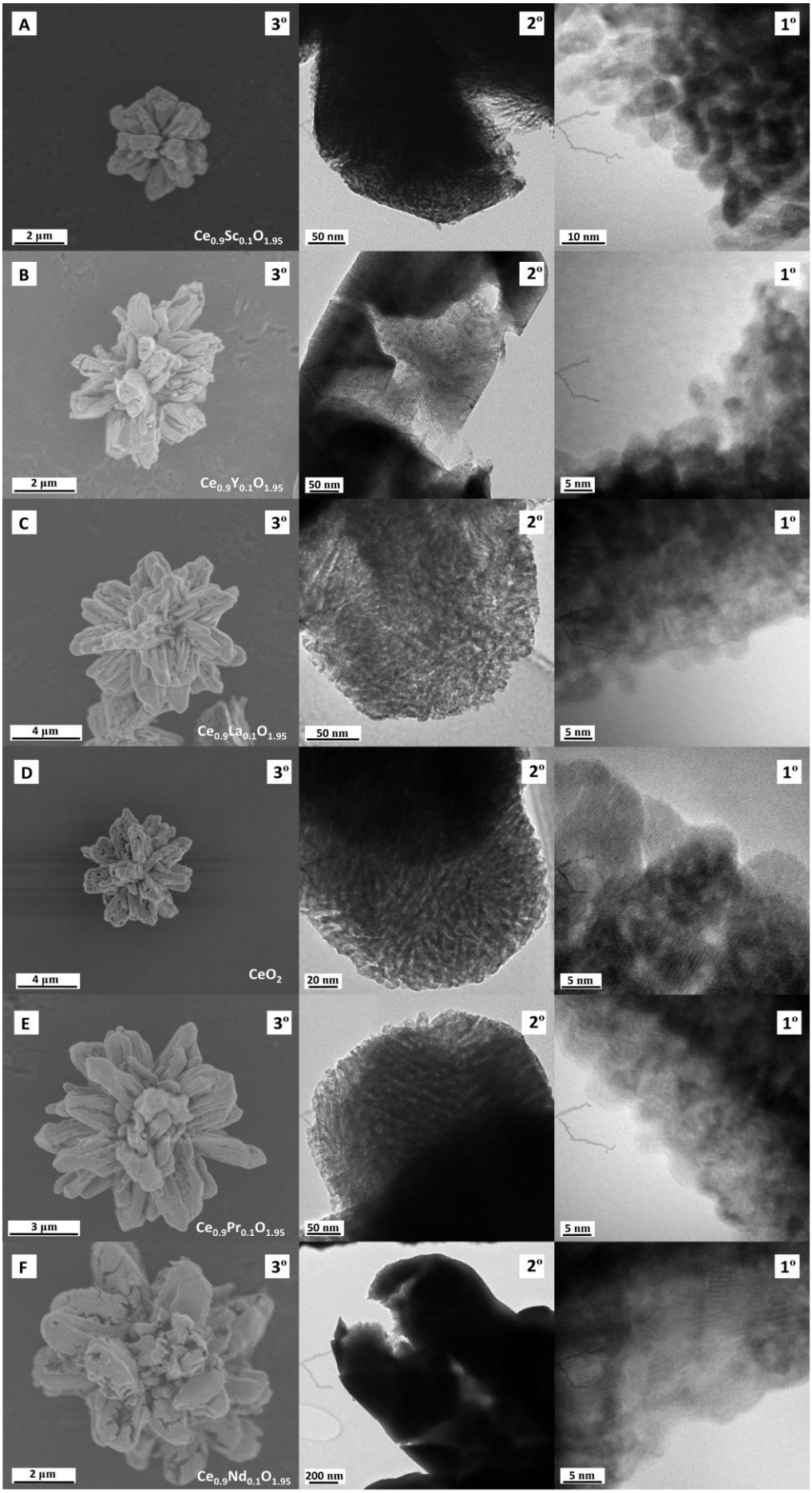
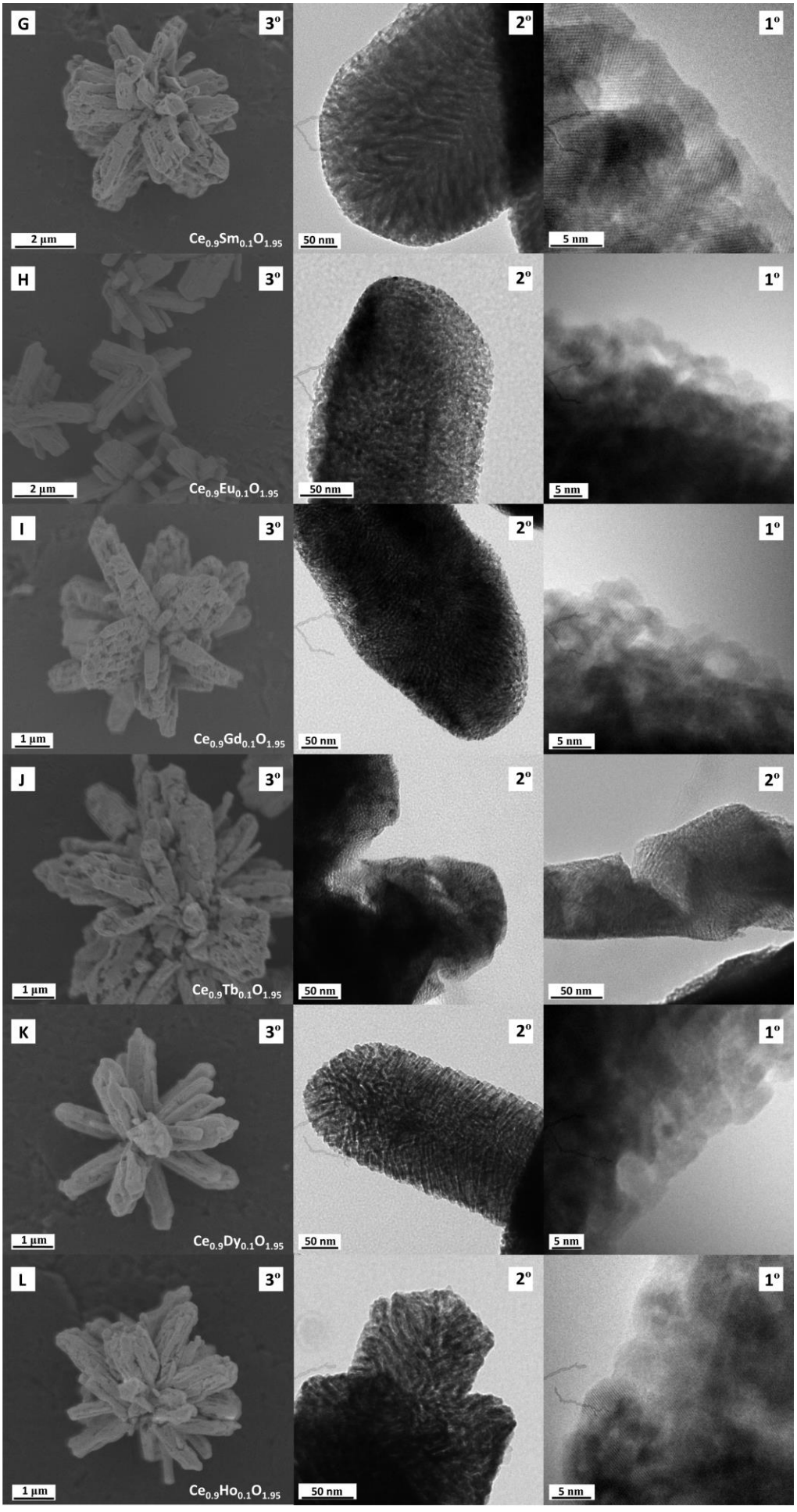


Fig S8. Ceria materials differed by 2nd hierarchy level organization of nanocrystallites; A. Undoped star-shaped particles (**CeO_2_Star**) heated at 550ºC; B. Gadolinium doped star-shaped particles, (**$Ce_{0.9}Gd_{0.1}O_{1.95}$_Star)** heated at 550ºC); C. Undoped star-shaped particles (**CeO_2_Star**) heated at 900ºC; D) Microemulsion-derived nanoparticles (**CeO_2_NPs**) heated at 550ºC; E. Microemulsion-derived nanoparticles (**CeO_2_NPs**) heated at 900ºC.


A
3º
2º
1º
2 µm
$Ce_{0.9}Sc_{0.1}O_{1.95}$
50 nm
10 nm
B
3º
2º
1º
2 µm
$Ce_{0.9}Y_{0.1}O_{1.95}$
50 nm
5 nm
C
3º
2º
1º
4 µm
$Ce_{0.9}La_{0.1}O_{1.95}$
50 nm
5 nm
D
3º
2º
1º
4 µm
CeO_2
20 nm
5 nm
E
3º
2º
1º
3 µm
$Ce_{0.9}Pr_{0.1}O_{1.95}$
50 nm
5 nm
F
3º
2º
1º
2 µm
$Ce_{0.9}Nd_{0.1}O_{1.95}$
200 nm
5 nm


G
3º
2 µm
$Ce_{0.9}Sm_{0.1}O_{1.95}$
2º
50 nm
1º
5 nm
H
3º
2 µm
$Ce_{0.9}Eu_{0.1}O_{1.95}$
2º
50 nm
1º
5 nm
I
3º
1 µm
$Ce_{0.9}Gd_{0.1}O_{1.95}$
2º
50 nm
1º
5 nm
J
3º
1 µm
$Ce_{0.9}Tb_{0.1}O_{1.95}$
2º
50 nm
2º
50 nm
K
3º
1 µm
$Ce_{0.9}Dy_{0.1}O_{1.95}$
2º
50 nm
1º
5 nm
L
3º
1 µm
$Ce_{0.9}Ho_{0.1}O_{1.95}$
2º
50 nm
1º
5 nm

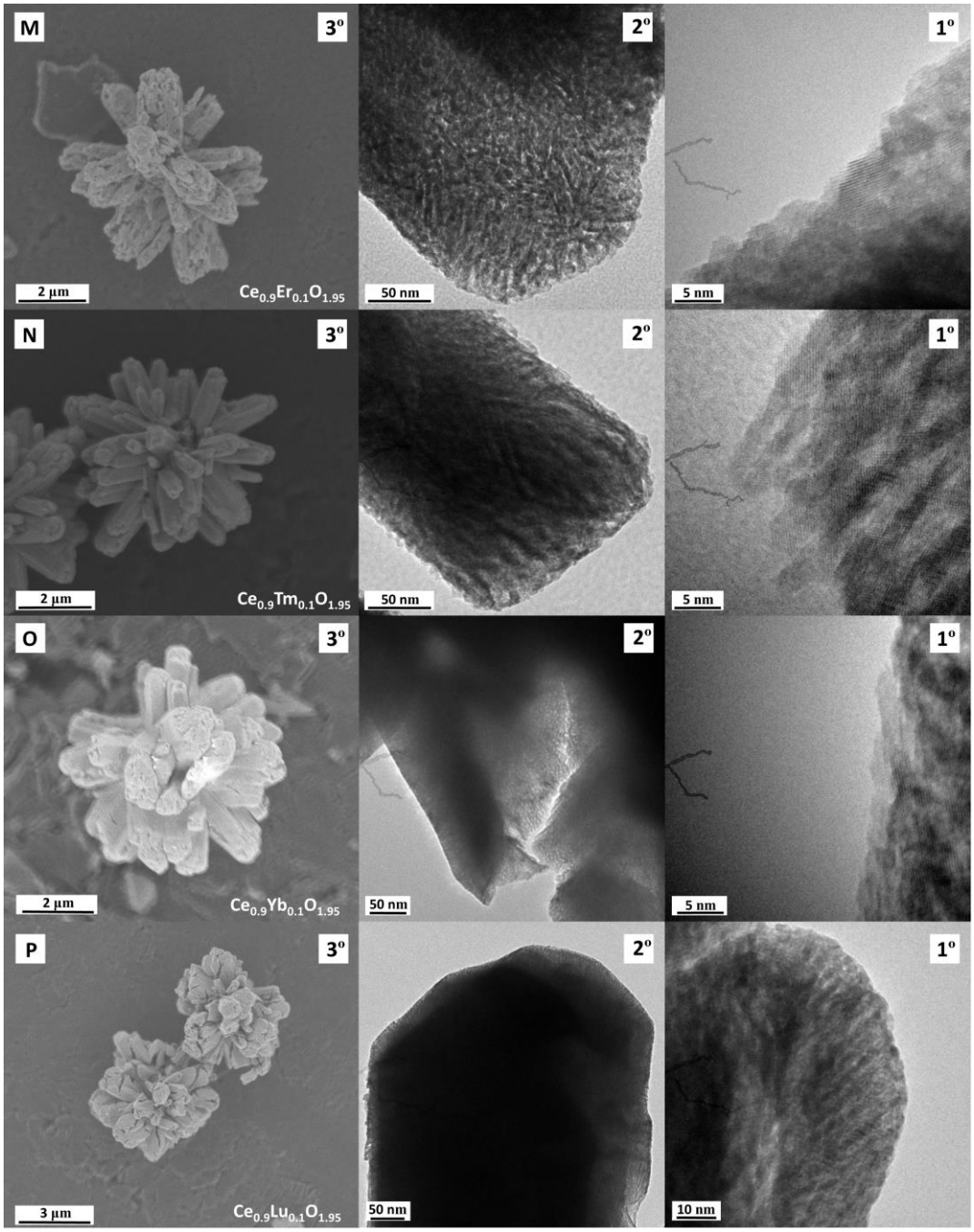


Fig S9. SEM and TEM images showing three-level hierarchical structure of star-like $Ce_{0.9}RE_{0.1}O_{1.95}$ mixed oxides particles; 1º 2º 3º - first, second and third hierarchy levels respectively; A) $Ce_{0.9}Sc_{0.1}O_{1.95}$ B) $Ce_{0.9}Y_{0.1}O_{1.95}$ C) $Ce_{0.9}La_{0.1}O_{1.95}$ D) CeO_2 E) $Ce_{0.9}Pr_{0.1}O_{1.95}$ F) $Ce_{0.9}Nd_{0.1}O_{1.95}$ G) $Ce_{0.9}Sm_{0.1}O_{1.95}$ H) $Ce_{0.9}Eu_{0.1}O_{1.95}$ I) $Ce_{0.9}Gd_{0.1}O_{1.95}$ J) $Ce_{0.9}Tb_{0.1}O_{1.95}$ K) $Ce_{0.9}Dy_{0.1}O_{1.95}$ L) $Ce_{0.9}Ho_{0.1}O_{1.95}$ M) $Ce_{0.9}Er_{0.1}O_{1.95}$ N) $Ce_{0.9}Tm_{0.1}O_{1.95}$ O) $Ce_{0.9}Yb_{0.1}O_{1.95}$ P) $Ce_{0.9}Lu_{0.1}O_{1.95}$.

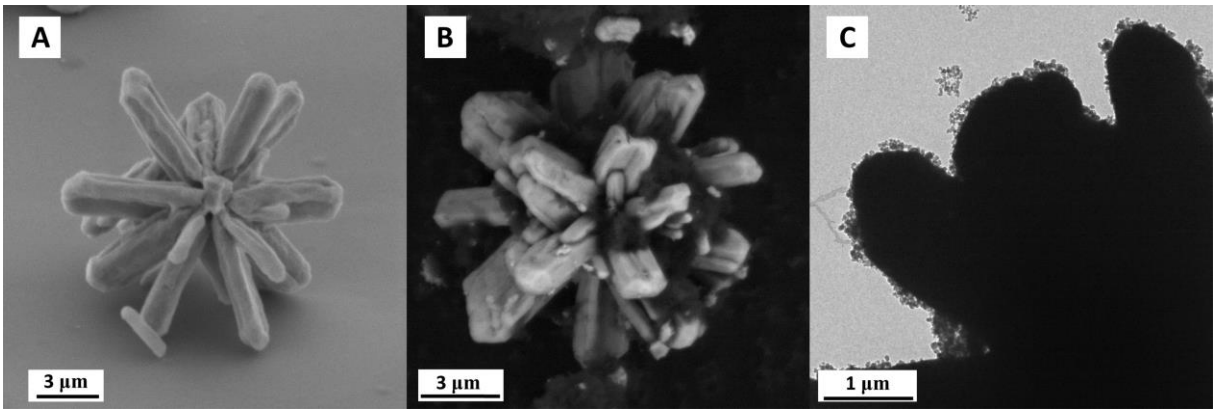


Fig S10. A) SEM image of CeO_2 star-shaped particles before mixing with soot; B) SEM image of CeO_2 star-sahaped particle after mixing with soot; C) TEM image of arms of CeO_2 star-shaped particle after mixing with soot.

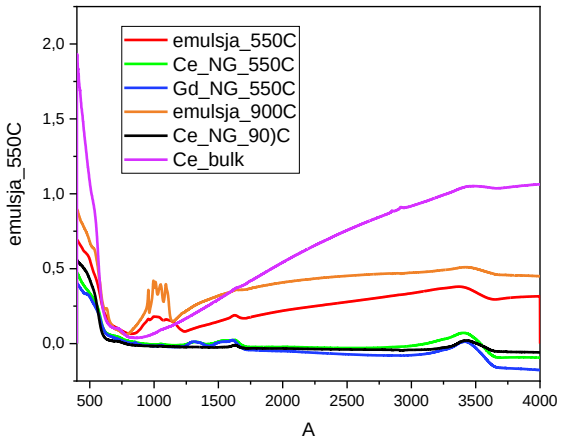


Fig. S11 FT-IR spectra of oxide samples heated at 550 ºC (before catalytic tests).

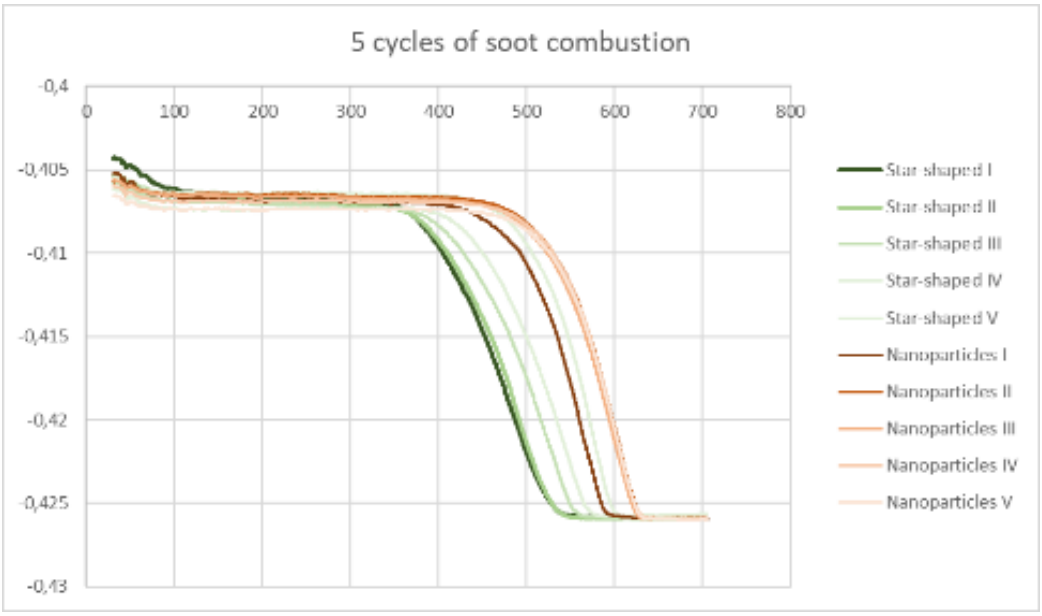


Fig. S12. Five cycles of soot combustion

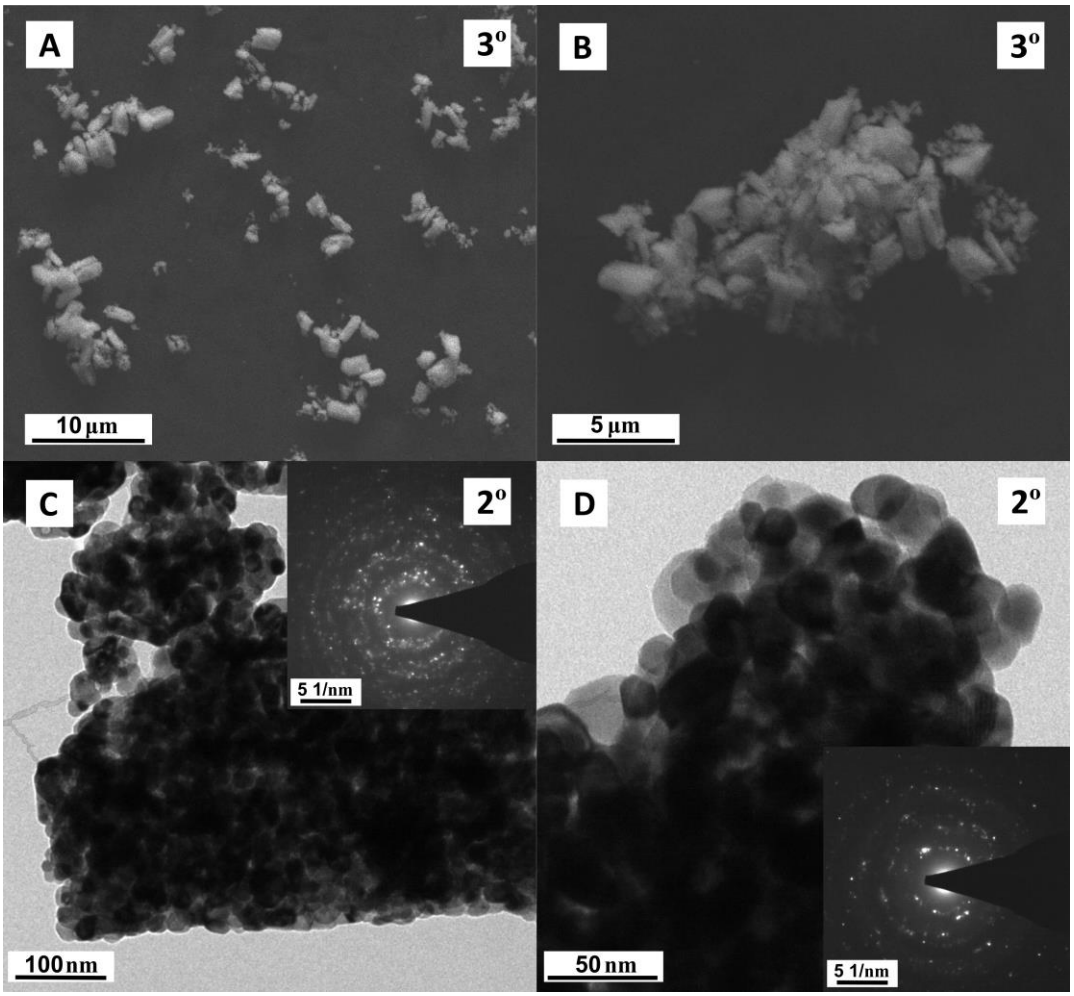


Fig. S13. SEM (A,B) and TEM (C,D) images of $CeO_{2-\delta}$_NG after 5th cycle of soot combustion. Loss of 3º (A, B) and 2º structure (inlet SAED patterns on images C and D) is observed.

Table S1. CeO_2 hierarchical architectures and CO oxidation catalytic performance

Ref.	Hierarchy description		T_{50} (ºC)	T_{50} of compartitive material (ºC)	Reactant feed	Space velocity (mL g^{-1} h^{-1})	BET (m^2/g)
[16]	3rd 2nd 1st	Nanobundles (0,5-1,2μm[b]/2-4μm[a]) Nanorods (<30nm) Nanoparticles(5.4 nm)[d]	213	261 (ceria nanoparticles)	5% CO, CO/O_2=0.15 in N_2	80000	130.4
[17]	3rd 2nd & 1st	Globin-like spheres (2-3 μm) Nano-sized building blocks interconnected by nanoparticles	162	272 (calcined cerium nitrate)	2% CO, 18% O_2, in N_2	18000	57.13
[20]	3rd 2nd 1st	Flowerlike spheres (5-8 μm) Nanowires (~6 nm)[c] Nanoparticles(~6 nm)	227	270 (bulk ceria)	1% CO, 20% O_2 in Ar	60000	64.2
[24]	3rd 2nd 1st	Spindle-like (2-5 μm)/ flower-like (5 μm) Nanoflakes Nanocrystallites (9.4 nm)	239	332 (commercial ceria)	1% CO, 1% O_2 in N_2	120000	171.6
[21]	3rd 2nd 1st	Flower-like (5 μm) Nanorods (20-40 nm[c]/1-2 μm[a]) –[e]	-	-	-	-	-
[18]	3rd 2nd 1st	Urchin-like (2.5-3 μm) Nanorods (50 nm[c]/1 μm[a]) –[e]	~400	~465 (commercial CeO_2)	1% CO, 10% O_2 in N_2	120000	115.2
[18]	3rd 2nd 1st	Coral-like (500-600 nm) Nanorods (50 nm[c]/ 200 nm[a] –[e]	~375	~465 (commercial CeO_2)	1% CO, 10% O2 in N2	120000	139.3
[22]	3rd 2nd 1st	Nanoflowers (250 nm) Nanorods (100 nm[a]/30 nm[c]) Nanocrystals (4.8 nm[d])	~230	-	1% CO, 10% O_2 in N_2	36000	95.7
[80]	3rd 2nd 1st	Nanoparticles (500 nm) Hollow nanocones Nanocrystallites (3-5 nm)	~200	~300 (commercial ceria)	1% CO, 10% O_2 in N_2	72000	147.6
[23]	3rd 2nd 1st	Microflowers (3 μm) Microrods (600nm[c]/2-3 μm[a]) Nanocrystallites (3-5 nm)	~230	~350 (commercial ceria)	1% CO, 10% O2 in N_2	96000	147.6
[19]	3rd 2nd	Sea urchin- like (10-50 μm) Rods (50 μm[a]/1-5	317	-	0.25% CO, 0.50% O_2 in N_2	96000	179 - 234

	1st	µm[c]) Nanocrystallites (10.3-14.7)					
[29]	3rd 2nd 1st	Flowerlike spheres (0,5- 10µm) Wrinkled petals Nanocrystallites (<10 nm)	~255 CeO_2 ~290 CeLa ~225 CePr	T_{20}=~400 (commercial ceria)	2% CO, 3% O_2 in N_2	60000	166 (CeO_2) 155 (CeLa) 140 (CePr)

[a] length, [b] width, [c] diameter, [d] mean grain size calculated by Scherrer equation, [e] no information