Supporting Information for:

Solvothermal Synthesis Routes to Substituted Cerium Dioxide Materials

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Table S1: Summary of rare-earth substituted cerium dioxide materials prepared by solvothermal synthesis

Rare-Earth substituent	**Composition $Ce_{1-x}Ln_xO_{2-\delta}$**	**Reagents**	**Synthesis conditions**	**Particle Morphology**	**Properties Tested**	**Reference**	**Notes**
La	Not stated	$Ce(NO_3)_3 \cdot 6H_2O$ $La(NO_3)_3 \cdot 6H_2O$ urea sodium citrate dehydrate water	120 °C 36 h	'broom-like' agglomerates of needles, length 5 μm, diameter ~200 nm	(i) photo degradation of aqueous bisphenol (ii) photocatalytic decomposition of gaseous acetaldehyde	[1]	Also applied for Ln = Nd, Sm and Y and properties compared
	5 wt%, 30 wt% 40 wt% La	$(NH_4)_2[Ce(NO_3)_6]$ $LaCl_3 \cdot 7H_2O$ acetic acid ethylene glycol water	180 °C 10 h 0.8 T magnetic field	nanoscale flakes or rods, with greater tendency for rod-shape in magnetic field	ferromagnetic response	[2]	
	x = 0.1	$Ce(NO_3)_3 \cdot 6H_2O$ $La(NO_3)_3 \cdot 6H_2O$ 11.5 M NaOH (aq)	180 °C 24 hours	~50 nm cubes	hydroxyl radical scavenging activity	[3]	
	x = 0.00, 0.03, 0.06, and 0.09	$(NH_4)_2[Ce(NO_3)_6]$ La_2O_3/HNO_3 KOH(aq)	100 °C 8 minutes microwave heating	6 – 12 nm spherical particles	photoluminescence	[4]	
	$0 \leq x \leq 0.25$	cerium (III) acetate hydrate	200 °C 3 hours	0.4–5 μm grain size after sintering	oxide-ion conductivity of sintered powders	[5]	Also used for Nd, Sm, Gd

		lanthanum (III) acetate hydrate triethylene glycol					
	x = 0.1	$CeCl_3 \cdot 7H_2O$ $LaCl_3$ NaCl 12 M NaOH(aq)	180 °C 24 hours	nanowires ~ 5 nm diameter, aspect ratio ~ 500, with (110) facets exposed	CO oxidation	[6]	Method applied to series of lanthanides La-Lu and CO oxidation optimised for Ln = Nd
	x = 0.091	$Ce(NO_3)_3 \cdot 6H_2O$ $La(NO_3)_3 \cdot 6H_2O$ hexamethylenetetramine water	80 °C 45 minutes	10–25 nm cube-shaped, stepped surface	-	[7]	
	$0 < x < 0.1$	$(NH_4)_2[Ce(NO_3)_6]$ $La(NO_3)_3 \cdot 6H_2O$ water	Up to 400 °C; continuous flow reactor	~7 nm isotropic crystallites	-	[8]	method also used for Pr
Pr	4, 8, 12% Pr	$(NH_4)_2[Ce(NO_3)_6]$ Pr_2O_3/HNO_3 KOH(aq)	100 °C 8 min microwave	5 to 15 nm diameter particles	photoluminescence	[9-10]	
	x = 0.5	$Ce(NO_3)_3 \cdot 6H_2O$ $Pr(NO_3)3 \cdot 6H_2O$ NaOH(aq)	180 °C 25 hours	rods and polyhedral particles < 100 nm diameter	CO conversion,soot combustion and total oxidation of volatile organics	[11]	Increased Pr content leads to rod-shaped particles
	x = 0.5	$Ce(NO_3)_3 \cdot 6H_2O$ $Pr(NO_3)3 \cdot 6H_2O$ NaOH(aq)	180 °C 24 hours	rods, 100 nm length, 20 nm diameter and cubes < 100 nm	CO, NO and soot oxidations (with Pt deposited on surface)	[12]	

	5, 10, 15, 20 mol %	$Ce(NO_3)_3 \cdot 6H_2O$ $Pr(NO_3)3 \cdot 6H_2O$ NaOH(aq)	180 °C 24 hours	nanocubes for ≤ 15 mol % Pr, nanocubes and nanorods for 20 mol % Pr	oxidation of 3,3′,5,5′-tetramethylbenzidine	[13]	
	10, 25, 50 mol %	$Ce(NO_3)_3 \cdot 6H_2O$ $Pr(NO_3)_3 \cdot 6H_2O$ NaOH(aq)	180 °C 24 hours	nanocubes for < 25 mol % Pr, nanocubes and nanorods for > 25 mol % Pr	soot combustion	[14]	
	x = 0.05, 0.1, 0.2	$Ce(NO_3)_3 \cdot 6H_2O$ $Pr(NO_3)3 \cdot 6H_2O$ NaOH(aq)	220 °C 24 hours	20–120 nm nanocubes, with rods at high Pr content	-	[15]	Same method used for Sm, Gd , Tb Orientated attachment model for crystallisation proposed
	x = 0.1, 0.2	$Ce(NO_3)_3 \cdot 6H_2O$ $Pr(NO_3)3 \cdot 6H_2O$ Urea Water	120 °C 1 hour microwave	200 nm spheres consisting agglomerates of smaller particles	Redox properties measured by heating in hydrogen	[16]	Also used for Gd
Nd	x ≤ 0.2	$(NH_4)_2[Ce(NO_3)_6]$ $Nd(NO_3)_3 \cdot 6H_2O$ Hexamethylenetetramine Water	90°C 1 hour	< 10 nm diameter primary particles, agglomerated	-	[17]	Method also used for Eu
	x = 0.1, 0.2	$Ce(NO_3)_3 \cdot 6H_2O$ $Pr(NO_3)3 \cdot 6H_2O$ NH_3(aq)	80 °C 4 hours	4-8 nm particles	ionic conductivity measured from sintered powders	[18]	Precipitate first prepared and washed and then returned to autoclave with water;

							also used for Sm and Gd
Sm	x = 0.1, 0.2	Cerium(III)acetate hydrate or $Ce(NO_3)_3 \cdot 6H_2O$ Samarium (III) acetate hydrate or $Sm(NO_3)_3 \cdot 6H_2O$ triethylene glycol	200 °C 5 hours	Micron-sized flakes	ionic conductivity measured from sintered powders	[19]	
	x= 0.1 – 0.3	$CeCl_3 \cdot 7H_2O$ Sm_2O_3 Polyvinylpyrrolidone HCl KClO3 N,N-dimethylformamide water	180 °C 4 hours	60 nm diameter spheres of smaller primary particles	CO oxidation	[20]	
	x = 0.091	$Ce(NO_3)_3 \cdot 6H_2O$ $Sm(NO_3)3 \cdot 6H_2O$ NH_3(aq)	100 °C followed by aging 0 °C for 45 days	120–150 nm diameter and 1–1.5 μm length rods	capacitance and ionic conductivity of deposited films of particles	[21]	
	x = 0.1, 0.15	$Ce(NO_3)_3 \cdot 6H_2O$ Sm_2O_3/HNO_3 NH_3(aq)	130°C (3 bar) for 20 min microwave	~ 7 nm cubes	catalytic oxidation of α-bisabolol	[22]	
	x = 0.1	$Ce(NO_3)_3 \cdot 6H_2O$ $Sm(NO_3)3 \cdot 6H_2O$ NaOH(aq)	180°C 24 hours	cubes 5 nm to 200 nm in size	-	[23]	Doping of ceria with rare earth elements of preferred +3 valence is found not to lower the amount of reduced Ce

							ions near the surfaces (EELS)
	x = 0.15	$Ce(NO_3)_3 \cdot 6H_2O$ $Sm(NO_3)3 \cdot 6H_2O$ KOH(aq)	200 °C 30 min microwave	~10 nm cuboid	ionic conductivity of sintered and densified pellets prepared from powder	[24]	Gd and mixed Gd, Sm materials also prepared
	x = 0.1	$Ce(NO_3)_3 \cdot 6H_2O$ $Sm(NO_3)3 \cdot 6H_2O$ NaOH(aq)	160 °C 24 hours	8–20 nm cubes	CO oxidation	[25]	Gd material also prepared
	x = 0 – 0.1	$Ce(NO_3)_3 \cdot 6H_2O$ $Sm(NO_3)3 \cdot 6H_2O$ 14 M NaOH(aq)	100 or 180 °C 24 h	Nanorods at 100 ^oC , 20 nm in diameter and average 200 nm in length Nanocubes at 180 ^oC	photoluminescent properties, optimised in cube crystals	[26]	
Eu	x = 0.03	$Ce(NO_3)_3 \cdot 6H_2O$ $Eu(NO_3)3 \cdot 6H_2O$ glycine NaOH(aq)	150 °C 10 hours	10–13 nm	photocatalytic degradation of congo red dye, and antibacterial properties	[27]	
	x = 0 – 0.4	$Ce(NO_3)_3 \cdot 6H_2O$ $Eu(NO_3)3 \cdot 6H_2O$ NaOH(aq)	180 °C 3 hours microwave	20-70 nm cubes	Reducibility measured by temperature programmed reduction	[28]	Smaller crystals with higher Eu content
	1–9 mol%	$Ce(NO_3)_3 \cdot 6H_2O$ $Eu(NO_3)3 \cdot 5H_2O$ epigallocatechin-3-gallate ethanol	120 - 180 °C 2 – 12 hours	hierarchical nanostructures: flower-like intergrown plates, microns thickness	photometric properties for visualization of latent fingerprints, and photodegradation of methylene blue	[29]	
	0.1 to 2 mol %.	$Ce(NO_3)_3 \cdot 6H_2O$ $Eu(NO_3)3 \cdot 5H_2O$	180 °C 12 hours	300–400 nm octahedra	enhanced light-harvesting efficiency of	[30]	

		trisodiumphosphate dodecahydrate water			dye-sensitised solar cells via downconversion of UV to visible light		
	0.3−50 atom %	$Ce(NO_3)_3 \cdot 6H_2O$ $Eu(NO_3)3 \cdot 5H_2O$ NH_3(aq) ethanol	180 °C 12 hours	pseudospherical with diameter 5 - 10 nm	luminescence	[31]	size decrease with increased europium concentration
Gd	x = 0.1	$Ce(NO_3)_3 \cdot 6H_2O$ $Gd(NO_3)3 \cdot 6H_2O$ 6-amino hexanoic acid *tert*-butylamine water	180 °C 24 hours	10 nm cubes, with {001} facets	composite with NiO prepared as anode in solid-oxide fuel cell with superior resistance	[32]	
	x = 0.1, 0.2	cerium (III) acetate hydrate gadolinium (III) acetate hydrate triethylene glycol	200 °C 3 hours	10-40 nm (from XRD peak broadening)	oxide-ion conductivity of sintered powders	[33]	
	x = 0.10, 0.15,0.20	$(NH_4)_2[Ce(NO_3)_6]$ $Gd(NO_3)3 \cdot 6H_2O$ hexamethylenetetramine water	180°C 5, 30, 60 min microwave	3-4 nm spherical	-	[34]	HMTA hydrolysis, which occurs upon heating of aqueous HMTA solutions to form formaldehyde and ammonia
	x = 0.1	$CeCl_3 \cdot 7H_2O$ $GdCl_3 \cdot 6H_2O$ octadecylamine ethanol	150 °C 72 hours	~24 nm by XRD peak broadening, aggregated	soot oxidation	[35]	

		ethylenediamine		nanocrystals from TEM			
						[36]	Gadolinium doped ceria on graphene cathode with enhanced cycle stability for non-aqueous lithium-oxygen batteries
	x = 0.2	$Ce(NO_3)_3 \cdot 6H_2O$ $Gd(NO_3)3 \cdot 6H_2O$ KOH(aq)	396°C for ~29 s followed by two down-stream stages at 290°C, and 285°C	6 - 40 nm with polyhedral or octahedral shape, depending on pH	processed into inks for inkjet printing and printed onto substrates suitable for solid-oxide fuel cell electrolyes	[37]	continuous flow-type apparatus: reagent solution and supercritical water mixed to induce crystallisation
	x = 0.1	$Ce(NO_3)_3 \cdot 6H_2O$ $Gd(NO_3)3 \cdot 6H_2O$ NH_3(aq) pH adjusted with HCl, water or KOH	140°C 1 day	10 nm cuboids	ionic conductivity of sintered pellets	[38]	
	x = 0.1, 0.2	$(NH_4)_2[Ce(NO_3)_6]$ $Gd(NO_3)3 \cdot 6H_2O$ tetramethyl ammonium hydroxide	240 °C 1 h	5 nm nanoparticles agglomerated into micron-sized particles	*in vivo* toxicity in rats studied	[39-40]	

		Water					
	x = 0.2	$Ce(SO_4)_2$ (aq) $Gd(NO_3)_3$(aq) $N(CH_3)_4OH$ $N(CH_3)_4HCO_3$	125−150°C 6−24 h	4 nm cubiodal	-	[41]	tetramethyl ammonium capping proposed to avoid agglomeration and ripening
	x = 0.05	Ce $(NO_3)_3 \cdot 6H_2O$ $Gd(NO_3)_3$(aq) water/ethylene glycol 1:7 vol:vol	350 or 380 °C 10 min	Spherical agglomerates of nanosheets 20–40 nm in thickness	CO oxidation	[42]	
	x = 0 or 0.15	$Ce(NO_3)_3 \cdot 6H_2O$ $Gd(NO_3)3 \cdot 6H_2O$ NH_3(aq)	250 °C 6–22 h neutral pH	8-15 nm	photoluminescence	[43]	Hydrothermal ripening of precipitate. Also used for Y
	x = 0.2	Ce $(NO_3)_3 \cdot 6H_2O$ $Gd(NO_3)_3$(aq) NH_3(aq)	130 °C 30 min microwave	nanorods 50–500 nm length 20–60 nm diameter	reforming of methanol	[44]	microwave heating accelerates the formation of nanorods
Tb	x = 0.1 or 0.2	Ce $(NO_3)_3 \cdot 6H_2O$ $Tb(NO_3)_3$(aq) urea water	120 °C 1 hour microwave	200 nm spheres of agglomerated 10 nm particles	redox properties on hydrogen reduction/ air oxidation	[45]	Tb^{4+} formation on reoxidation
	x = 0.1, 0.2 and 0.3)	Ce $(NO_3)_3 \cdot 6H_2O$ $Tb(NO_3)_3$(aq) urea water	microwave treated: 800 W for 3 x 1 minute	not stated	red ceramic pigments	[46]	also mixed Tb,Y materials prepared

Dy	x = 0.1	$Ce(NO_3)_3 \cdot 6H_2O$ $Dy(NO_3)_3 \cdot nH_2O$ NH_3(aq)	120 °C 12 h	~25 nm from XRD peak broadening	temperature programmed reduction (H_2) and CO oxidation	[47]	All Ln, La-Yb studied by same method
Ho	x = 0.1	$Ce(NO_3)_3 \cdot 6H_2O$ $Ho(NO_3)_3 \cdot 5H_2O$ NH_3(aq)	120 °C 12 h	~25 nm from XRD peak broadening	temperature programmed reduction (H_2) and CO oxidation	[47]	All Ln, La-Yb studied by same method
Er	x = 0.091	$Ce(NO_3)_3 \cdot 6H_2O$ $Er(OCOCH_3)_3 \cdot 4H_2O$ formic acid methanol	300 °C 10 minutes	mesoporous spheres, ~ 150 nm diameter	luminescence	[48]	Supercritical conditions; also mixed Er,Yb
	x = 0.01-0.007	$Ce(NO_3)_3 \cdot 6H_2O$ $Er(NO_3)3 \cdot 5H_2O$ $LiNO_3$ $Na_3PO_4 \cdot 12H_2O$ water	180 °C for 12 h	octahedra with 50 to 100 nm edges	Vis-NIR emission under optical up-and down-conversion excitation; enhanced emission when Li is present.	[49]	Morphology maintained on 800 °C annealing. Li co-doped?
	0, 0.2, 0.3,0.4 and 0.5 wt% Er	$Ce(NO_3)_3$ (aq) $Er(NO_3)_3$(aq) 0.1 M NaOH	120 °C 8 h	Agglomerated particles, 10s of nm in dimension	Photodegradation of Rhodamine-B, and antimicrobial performance	[50]	
	$x \leq 0.5$	$Ce(NO_3)_3$ (aq) $Er(NO_3)_3$(aq) ~9 M NaOH	220 °C 24 h Or 220 °C 6 h (microwave)	Cube-shaped particles, 10s of nm in dimension, with bimodal size distribution	-	[51]	$Er(OH)_3$ impurity found for x >0.3 in microwave synthesis
	x = 0.0625 – 0.5	$Ce(NO_3)_3$ (aq) $Er(NO_3)_3$(aq) $Na_3PO_4 \cdot 12H_2O$	190 °C 12 hours	200 – 300 nm octahedral	photoluminescence	[52]	

		water					
Tm	x = 0.1	$Ce(NO_3)_3 \cdot 6H_2O$ $Tm(NO_3)_3 \cdot 5H_2O$ NH_3(aq)	120 °C 12 h	~25 nm from XRD peak broadening	temperature programmed reduction (H_2) and CO oxidation	[47]	All Ln, La-Yb studied by same method
Yb	x = 0 - 0.50	$Ce(NO_3)_3 \cdot 6H_2O$ $Yb(NO_3)_3 \cdot 6H_2O$ NaOH, or $Na_3PO_4 \cdot 12H_2O$ water	220 or 170 °C 24 or 12 h (or 220 or 170 °C, 3 hours, microwave)	~ 10 -15 nm cubes (from NaOH) ~10 - 50 nm octahedral from $Na_3PO_4 \cdot 12H_2O$	soot oxidation	[53] [54]	YbO(OH) impurity in x = 0.5 materials
Lu	x = 0.1	$CeCl_3 \cdot 7H_2O$ $LuCl_3$ NaCl 12 M NaOH(aq)	180 °C 24 hours	nanowires ~ 5 nm diameter, aspect ratio ~ 500, with (110) facets exposed	CO oxidation	[6]	Method applied to series of lanthanides La-Lu and CO oxidation optimised for Ln = Nd
Y	x = 0.091	$Ce(NO_3)_3 \cdot 6H_2O$ $Y(NO_3)_3 \cdot 6H_2O$ polystyrene microspheres water	150 °C 24 h	200 nm hollow spheres	Photocatalytic activity for acetaldehyde decomposition	[55]	
	x = 0.08	$Ce(NO_3)_3 \cdot 6H_2O$ $Y(NO_3)_3 \cdot 6H_2O$ Na_3PO_4 water	100–250 °C for 12–96 h	200 nm octahedral with nanorod coating with increasing Na_3PO_4	Photocatalytic activity for acetaldehyde decomposition	[56]	
	x = 0.11	$Ce(NO_3)_3 \cdot 6H_2O$ $Y(NO_3)_3 \cdot 6H_2O$	110°C	nanorods	Photocatalytic degradation of dyes	[57]	Increasing $Y(OH)_3$

		NaOH(aq)	24 h	100±37 nm in length and 10.9±2.8 nm in diameter			impurity with higher attempted Y inclusion

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