Supplementary Material (ESI) for Journal of Materials Chemistry

Dramatic reduction of the oxygen vacancy formation energy in ceria particles: A possible key to their remarkable reactivity at the nanoscale

Electronic Supplementary Information

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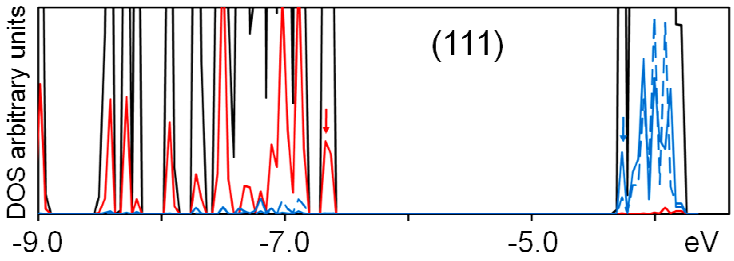

Fig. ESI1 Total (black line) and partial density of states (DOS) of the CeO_2(111) surface in absolute energy scale (cf. Fig. 9). Red – 2p DOS of the O atom removed (according to M. V. J. Ganduglia-Pirovano, L. F. Da Silva, J. Sauer, *Phys. Rev. Lett.*, 2009, **102**, 026101) with the lowest E_f, blue – 4f DOS of the two Ce^{4+} cations reduced by electrons of the O^{2-} anion during its depletion. Arrows mark boundary states dominated by the O (red) and Ce (blue) atoms involved in the O_{vac} formation. The Kohn-Sham energies are adjusted by the vacuum potential value normal to the (111) surface.

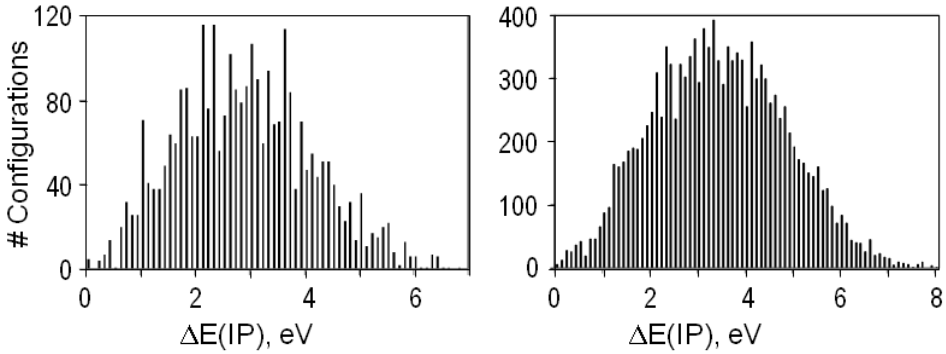

Fig. ESI2 Distribution of the 2940 and 13050 O_{vac} configurations derived from (left) $Ce_{21}O_{42}$ and (right) $Ce_{30}O_{59}$, respectively, as a function of the relative energy.

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Table ESI1 PW91+4 structural parameters and descriptors for the pristine Ce_nO_{2n} and defective Ce_nO_{2n-1} (n=21, 30, 40, 80) NPs, and CeO_2 slab with steps. E_f^{PW91+4} is the energy involved in the formation of a single oxygen vacancy O_{vac} in the NPs and slab model with steps; Ce-O is the average distance between the depleted O atom and its coordinated Ce atoms in the pristine systems; $D(O_{vac})$ is the total displacement of the Ce atoms first-neighbours to O_{vac} defined in the main text; Ce^{3+}-O is the average distance between the reduced Ce^{3+} cation and its coordinated O atoms in the defective systems. Position, type and coordination of Ce^{3+} cations: NX (X=1, 2 etc.) indicates first-, second-neighbour site, etc.; c, e, f, i indicate corner, edge, facet, and inside sites, respectively. Distances are in pm, energies are in eV.

Model	O_{vac}	E_f^{PW91+4}	Ce-O	$D(O_{vac})$	#1 Ce^{3+}					#2 Ce^{3+}				
					Position	Type	Coord.	Ce^{3+}-O	Δ_{Ce3+-O}	Position	Type	Coord.	Ce^{3+}-O	Δ_{Ce3+-O}
$Ce_{21}O_{42}$	edge O_{2c}	2.44	217	98	N1	c	Ce_{5c}^{a}	226	4	N1	c	Ce_{5c}^{b}	229	6
	edge O_{2c}	1.99	215	66	N1	c	Ce_{5c}^{c}	227	4	N1	c	Ce_{5c}^{b}	227	4
	edge O_{2c}	1.98		67	N1	c	Ce_{5c}^{c}	228	4	N2	f	Ce_{6c}	239	12
	edge O_{2c}	2.19	215	59	N2	c	Ce_{5c}^{d}	237	14	N3	c	Ce_{5c}^{a}	236	13
	edge O_{2c}	2.12		60	N3	c	Ce_{5c}^{d}	236	13	N2	c	Ce_{5c}^{e}	237	14
	edge O_{2c}	2.10		54	N1	c	Ce_{6c}	231	4	N1	c	Ce_{6c}	231	4
	edge O_{2c}	2.04		59	N2	c	Ce_{5c}^{a}	237	14	N2	c	Ce_{5c}^{e}	237	14
	edge O_{2c}	1.67		67	N2	e	Ce_{6c}^{f}	229	12	N3	e	Ce_{6c}^{g}	229	16
	sub-facet O_{4c}	2.25	233	94	N3	c	Ce_{5c}^{d}	236	13	N2	c	Ce_{5c}^{a}	237	14
	sub-facet O_{4c}	2.15		95	N3	c	Ce_{5c}^{d}	236	13	N2	c	Ce_{5c}^{e}	237	14
	sub-facet O_{4c}	2.05		92	N2	c	Ce_{5c}^{a}	236	14	N2	c	Ce_{5c}^{e}	236	14
	sub-facet O_{4c}	1.98		103	N1	e	Ce_{6c}^{f}	238	10	N2	c	Ce_{5c}^{e}	236	14
	sub-facet O_{4c}	1.82		104	N1	e	Ce_{6c}^{f}	238	10	N2	e	Ce_{6c}^{g}	241	13
$Ce_{30}O_{60}$	edge O_{2c}	2.06	215	74	N1	c	Ce_{5c}^{h}	227	4	N1	c	Ce_{5c}	227	3
	edge O_{2c}	2.02		62	N1	c	Ce_{5c}^{h}	234	10	N2	f	Ce_{5c}^{i}	243	16
	edge O_{2c}	1.89		57	N2	c	Ce_{5c}^{j}	236	13	N2	f	Ce_{5c}^{i}	241	13
	edge O_{2c}	1.56	217	79	N3	c	Ce_{5c}^{j}	237	14	N3	c	Ce_{5c}^{k}	238	16
	edge O_{2c}	1.54		80	N2	c	Ce_{5c}^{j}	236	13	N3	c	Ce_{5c}	238	15
	facet O_{3c}	3.11	231	110	N3	c	Ce_{5c}^{j}	237	14	N3	c	Ce_{5c}^{k}	236	14
	facet O_{3c}	2.77		125	N1	e	Ce_{6c}	235	5	N1	f	Ce_{7c}^{l}	238	5
	sub-facet O_{4c}	2.71	232	80	N4	c	Ce_{5c}^{j}	236	13	N2	c	Ce_{5c}^{k}	240	17
	sub-facet O_{4c}	2.68		104	N1	e	Ce_{6c}^{m}	237	9	N1	f	Ce_{7c}^{l}	240	7
	sub-facet O_{4c}	2.43		102	N1	e	Ce_{6c}^{m}	237	8	N1	e	Ce_{6c}	238	8
	inside O_{4c}	1.68	237	101	N3	c	Ce_{5c}^{j}	236	13	N2	c	Ce_{5c}	238	15
	inside O_{4c}	1.59		104	N3	c	Ce_{5c}^{j}	236	13	N3	c	Ce_{5c}^{k}	238	9
$Ce_{40}O_{80}$	edge O_{2c}	1.57	216	67	N1	c	Ce_{5c}	236	5	N1	c	Ce_{5c}	237	24
	edge O_{2c}	0.83		70	N3	e	Ce_{5c}	240	9	N3	c	Ce_{4c}^{n}	227	14
	edge O_{2c}	0.80		72	N4	c	Ce_{4c}^{o}	226	13	N3	c	Ce_{4c}^{n}	227	14
	facet I O_{3c}	2.67	236	77	N4	c	Ce_{4c}^{o}	226	13	N1	c	Ce_{3c}^{n}	216	3
	facet II O_{3c}	2.50	236	78	N1	e	Ce_{5c}	235	4	N1	e	Ce_{6c}	239	5
	facet II O_{3c}	1.96		94	N2	c	Ce_{4c}^{o}	227	14	N5	c	Ce_{4c}^{n}	227	14
	facet III O_{3c}	1.82	235	89	N3	c	Ce_{4c}^{o}	227	14	N3	c	Ce_{4c}^{n}	227	14
	sub-facet O_{4c}	2.16	233	82	N5	c	Ce_{4c}^{o}	227	14	N2	c	Ce_{4c}^{n}	227	14
	sub-facet O_{4c}	1.22	231	92	N4	c	Ce_{4c}^{o}	227	14	N1	e	Ce_{6c}	244	9
	sub-facet O_{4c}	1.05		86	N4	c	Ce_{4c}^{o}	225	12	N3	c	Ce_{4c}^{n}	227	14
	inside O_{4c}	1.79	234	86	N3	c	Ce_{4c}^{o}	227	14	N4	c	Ce_{4c}^{n}	227	14
$Ce_{80}O_{160}$	edge O_{2c}	1.52	216	66	N1	c	Ce_{6c}	235	4	N1	c	Ce_{6c}	235	5
	edge O_{2c}	0.46		68	N4	c	Ce_{4c}^{p}	228	14	N2	e	Ce_{6c}^{q}	243	12
	edge O_{2c}	0.74	218	67	N8	c	Ce_{4c}^{p}	228	14	N6	e	Ce_{6c}^{q}	243	12
	edge O_{2c}	0.58		67	N8	c	Ce_{4c}^{p}	228	14	N7	e	Ce_{6c}	243	12
CeO_2 slab with steps	edge O_{2c}	1.50	226	28	N2	f	Ce_{7c}	246	11	N1	e	Ce_{5c}	224	2

[a] Same Ce^{3+} site; [b] Same Ce^{3+} site; [c] Same Ce^{3+} site; [d] Same Ce^{3+} site; [e] Same Ce^{3+} site; [f] Same Ce^{3+} site; [g] Same Ce^{3+} site; [h] Same Ce^{3+} site; [j] Same Ce^{3+} site; [k] Same Ce^{3+} site; [l] Same Ce^{3+} site; [m] Same Ce^{3+} site; [n] Same Ce^{3+} site; [o] Same Ce^{3+} site; [p] Same Ce^{3+} site; [q] Same Ce^{3+} site.

Table ESI2 Potential parameters employed in the present work according to ref. 34-36, as discussed in the manuscript.

Short-Range Potential Parameters: $V(r)=A\exp(-r/\rho)-C/r^6$			
	A (eV)	ρ (Å)	C (eV/Å^6)
O^{2-}-O^{2-}	22764.3	0.149	43.83
Ce^{4+}-O^{2-}	1986.83	0.35107	20.4
Ce^{3+}-O^{2-}	1731.61808	0.3535	14.43256
Shell Model Parameters: $V(r)=k_2r^2$			
	Shell charge (e)	k_2 (eVÅ^{-2})	
O^{2-}	-2.08	27.29	
Ce^{4+}	7.70	291.75	
Ce^{3+}	7.70	291.75	