

Fluoride-assisted detection of glutathione by surface Ce³⁺/Ce⁴⁺ engineered nanoceria

Vaishwik Patel¹, Linta Jose¹, Gilles Philippot², Cyril Aymonier², Talgat Inerbaev^{3,4}, Luke R. McCourt⁵, Michael G. Ruppert⁵, Dongchen Qi⁶, Wei Li⁶, Jiangtao Qu⁷, Rongkun Zheng⁷, Julie Cairney⁷, Jiabao Yi¹, Ajayan Vinu^{1*}, Ajay S. Karakoti^{1*}

¹Global Innovative Center for Advanced Nanomaterials (GICAN), School of Engineering College of Engineering, Science and Environment, The University of Newcastle, Callaghan, NSW, 2308, Australia

²Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France

³L. N. Gumilyov Eurasian National University, Nur-Sultan 010008, Kazakhstan

⁴Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk 630090, Russia

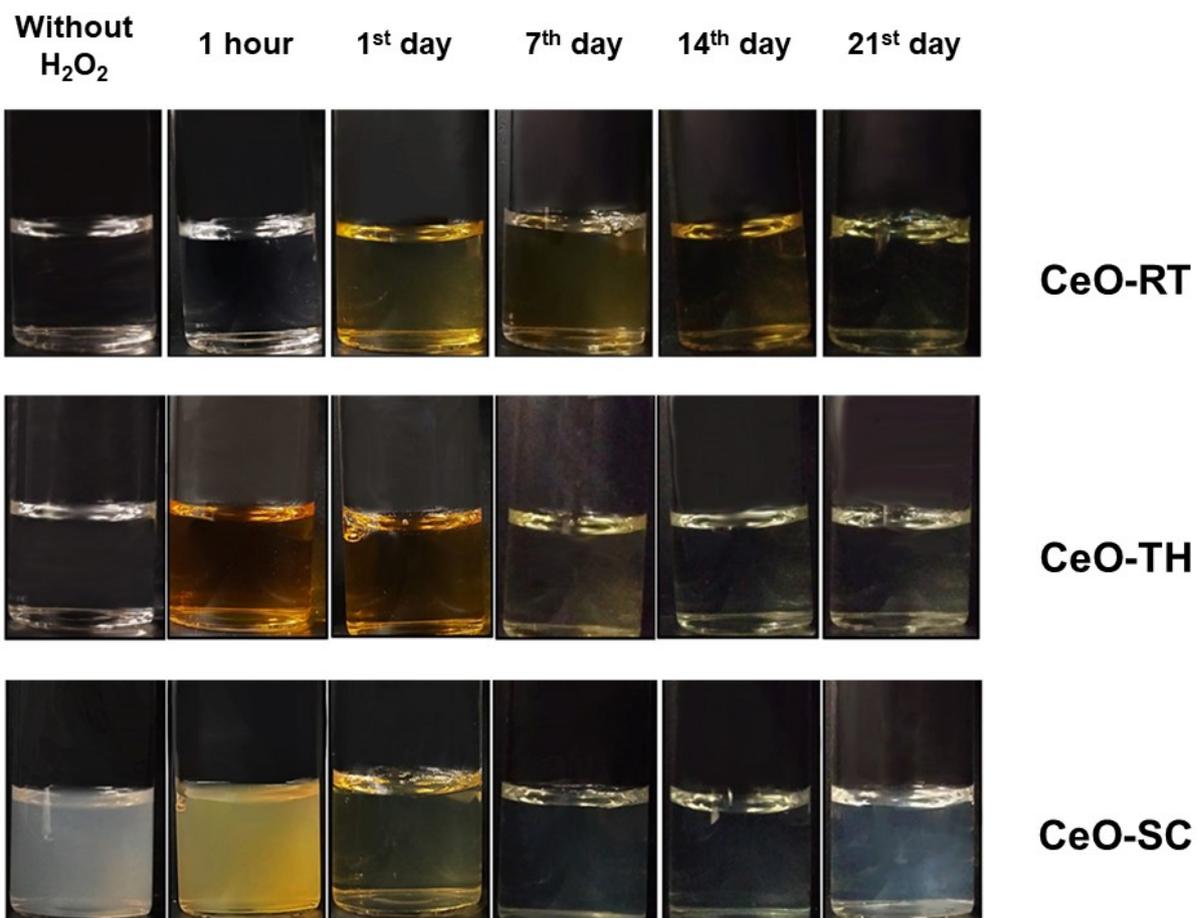
⁵School of Engineering, College of Engineering, Science and Environment, The University of Newcastle, Callaghan, 2308, Australia

⁶Centre for Materials Science, School of Chemistry and Physics, Queensland University of Technology, Brisbane, QLD 4001, Australia

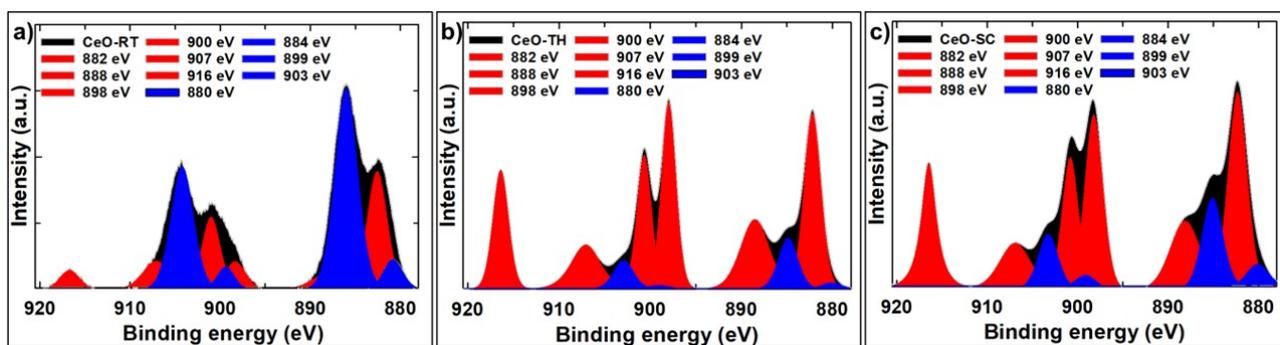
⁷School of Physics, The University of Sydney, NSW, 2000, Australia

* Corresponding author. Global Innovative Center for Advanced Nanomaterials (GICAN), School of Engineering, College of Engineering, Science and Environment, The University of Newcastle, Callaghan, NSW, 2308, Australia

Email address: ajayan.vinu@newcastle.edu.au, ajay.karakoti@newcastle.edu.au

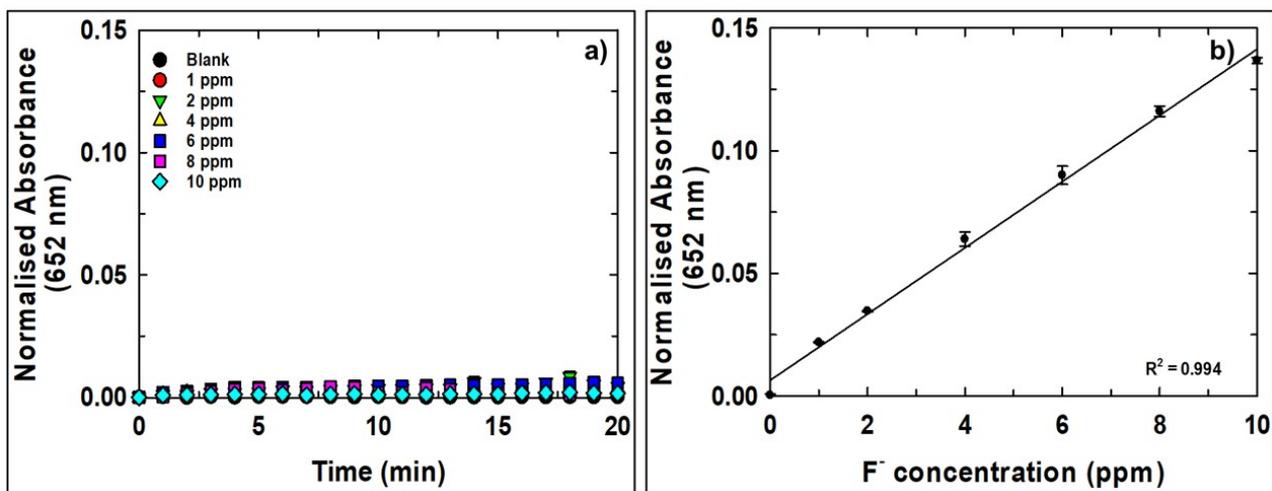


ESI 1: Change in the colour (representative of oxidation states) of nanoceria synthesised via different routes after a treatment with H_2O_2 and monitored for 21 days

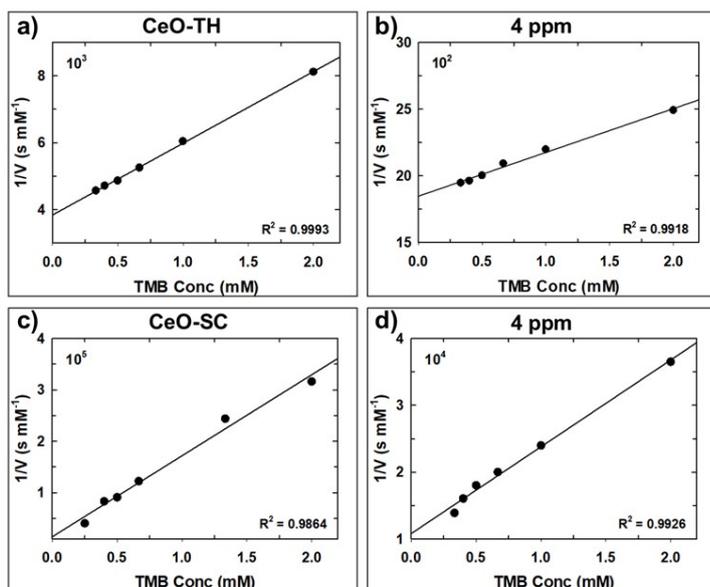


ESI 2: Deconvoluted XPS spectrum of as synthesized a) CeO-RT, b) CeO-TH, and c) CeO-SC

Peak	state	peak position	CeO-RT		CeO-TH		CeO-SI		CeO-TH-T		CeO-SI-T	
			FWHM	Peak %	FWHM	Peak %	FWHM	Peak %	FWHM	Peak %	FWHM	Peak %
v	Ce ⁴⁺	882	2.6	15.61	2.2	20.44	2.5	20.24	2.3	21.54	2.5	20.17
v''	Ce ⁴⁺	888	5.6	0.28	3.7	13.55	3.9	11.03	3.8	13.22	4.1	11.68
v'''	Ce ⁴⁺	898	2.6	4.15	1.9	18.75	2.4	17.33	1.9	18.61	2.4	17.3
u	Ce ⁴⁺	901	2.1	7.49	1.93	13.65	2.1	11.86	2.0	12.88	2.4	12.46
u''	Ce ⁴⁺	907	3.1	3.43	3.8	8.91	4.0	7.47	3.8	8.95	4.0	7.91
u'''	Ce ⁴⁺	916	2.5	2.65	2.0	12.7	2.0	11.74	2.0	12.8	2.1	11.72
v ⁰	Ce ³⁺	880	2.5	3.42	2.5	0.83	2.9	2.65	2.7	1.32	2.5	2.69
v'	Ce ³⁺	884	3.4	37.44	2.5	6.75	2.7	10.16	2.5	6.06	2.4	8.85
u ⁰	Ce ³⁺	899	2.2	2.99	2.7	0.51	2.8	1.64	2.9	0.81	2.5	1.66
u'	Ce ³⁺	903	3.4	22.55	2.6	3.9	2.6	5.87	2.4	3.81	2.7	5.56
Total Ce ⁴⁺ (%)			33.61		88.00		79.67		88.00		81.24	



ESI 4: a) Effect of fluoride ion on oxidation of TMB, b) Linear range of detection of fluoride ions within 1-10 ppm by CeO-SC

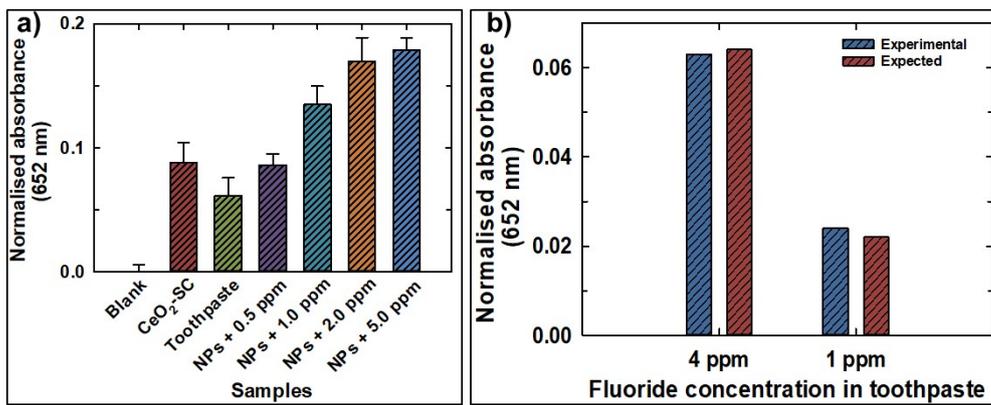


	Km	Vmax
CeO-TH	0.56	2.6*10 ⁻⁷ M sec ⁻¹
CeO-TH-F (4 ppm)	0.18	5.4*10 ⁻⁷ M sec ⁻¹
CeO-SC	10.99	6.98*10 ⁻⁸ M sec ⁻¹
CeO-SC-F (4 ppm)	1.2	9.25*10 ⁻⁸ M sec ⁻¹

ESI 5: Enzyme kinetics representation for TMB through Lineweaver-Burk plot of a) CeO-TH, b) CeO-TH-F⁻ (4 ppm), c) CeO-SC, d) CeO-SC-F⁻ (4 ppm).

ESI 6: Zetapotential of fluoride treated and untreated CeO-RH, CeO-TH and CeO-SC nanoparticles

Samples	AVG (mV)	STD
CeO-RT	+44.2	0.9
CeO-RT-F	+42.0	1.1
CeO-TH	+43.0	1.6
CeO-TH-F	+42.0	0.6
CeO-SC	+42.8	0.3
CeO-SC-F	+38.0	1.3



ESI 7: a) Fluoride detection with spiking of known concentration in toothpaste solution and b) Comparison of data obtained from toothpaste solution (without spiking).