Electronic Supplementary Information

Fluoride-capped nanoceria as highly efficient oxidase-mimicking nanozyme: inhibiting product adsorption and increasing oxygen vacancy

Yilin Zhao[1,2], Yawen Wang[2], Avi Mathur[2], Yaoqiang Wang[1], Vivek Maheshwari[2], Haijia Su[1]*, Juewen Liu[2]*

[1] Beijing Key Laboratory of Bioprocess, Beijing University of Chemical Technology (BUCT), 15 BeiSanhuan East Road, ChaoYang District, Beijing, 100029, P. R. China.
Email: suhj@mail.buct.edu.cn

[2] Department of Chemistry, Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.
Email: liujw@uwaterloo.ca

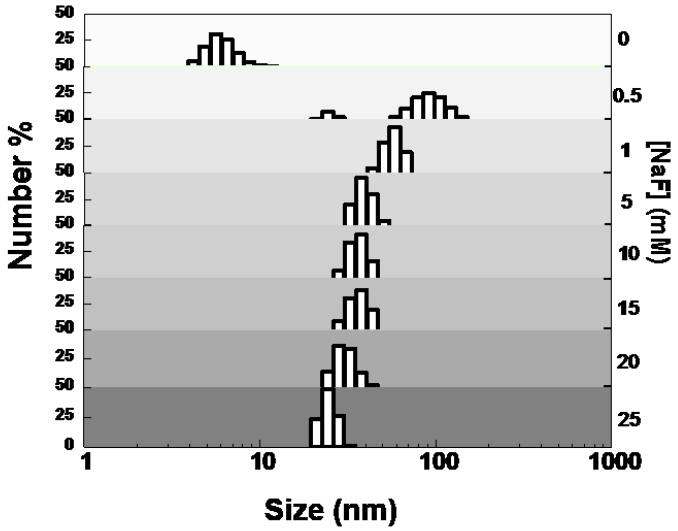

Figure S1. The hydrodynamic diameters of the CeO_2 NPs (200 μg mL^{-1}) as a function of F^- concentration at pH 4 (acetate buffer, 25 mM) measured by DLS.

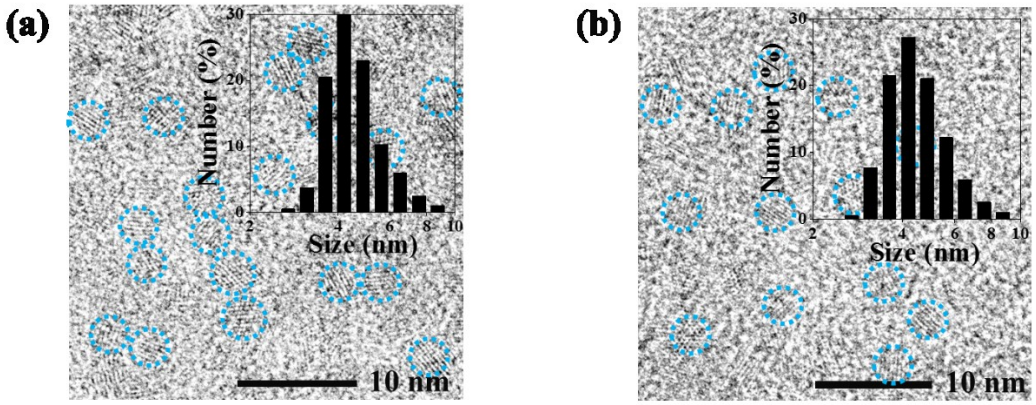

Figure S2. The HRTEM micrographs and hydrodynamic diameters of the CeO_2 NPs (200 μg mL^{-1}) (a) before and (b) after reaction with 5 mM F^- and 0.5 mM ABTS at pH 4 (acetate buffer, 25 mM). After reaction, the precipitates were washed 3 times after adding phosphate (500 mM, 5 μL) to desorb the oxidation product of ABTS and F^- before drying on TEM grids and imaging.

Table S1. Thermodynamic parameters from ITC fitting.

Sample	N	K_a ($\times 10^3$ M^{-1})	K_d (mM)	ΔG(kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔS (cal K^{-1} mol^{-1})
F^-	316±56.6	[a] 1.8 ± 0.3	0.56 ± 0.14	-4.4 ± 2.5	-11.0 ± 2.5	-21.9
Cl^-	8.53±14	[b] 1.1 ± 0.3	----	----	----	----
Br^-	8.91±29	[b] 1.3 ± 0.7	----	----	----	----
I^-	6.96±31	[b] 1.6 ± 0.8	----	----	----	-----
PO_3^{3-}	181±7.95	[a] 29.6 ± 1.4	0.03 ±0.002	-6.1 ± 0.6	-4.8 ± 0.6	4.25

[a]: The binding data were obtained using a one-site binding model.
[b]: Binding (K_a < 1000 M^{-1}) was not detectable by ITC.

Table S2. A comparison of the steady-state enzyme kinetic parameters of bare nanoceria and 1 mM F^- treated nanoceria (F^-–CeO_2). The CeO_2 NP concentration refers to the particle concentration. Data from Ref. 28 in the main paper.

Sub	CeO_2 (nM)	V_{max}[a] (μMs^{-1})	K_m[b] (mM)	k_{cat}[c] (s^{-1})	k_{cat}/K_m (s^{-1} mM^{-1})
ABTS	430	1.20	0.18	2.80	12.56
ABTS+F^-	43	0.55	0.062	12.84	207.10
TMB	430	0.069	1.50	0.16	0.11
TMB+F^-	43	0.063	0.14	1.47	10.47

[a]: V_{max} is the maximal reaction velocity
[b]: K_m is the Michaelis constant
[c]: k_{cat} is the catalytic constant. $k_{cat} = V_{max}/[E]$, and [E] is the concentration of nanoceria.

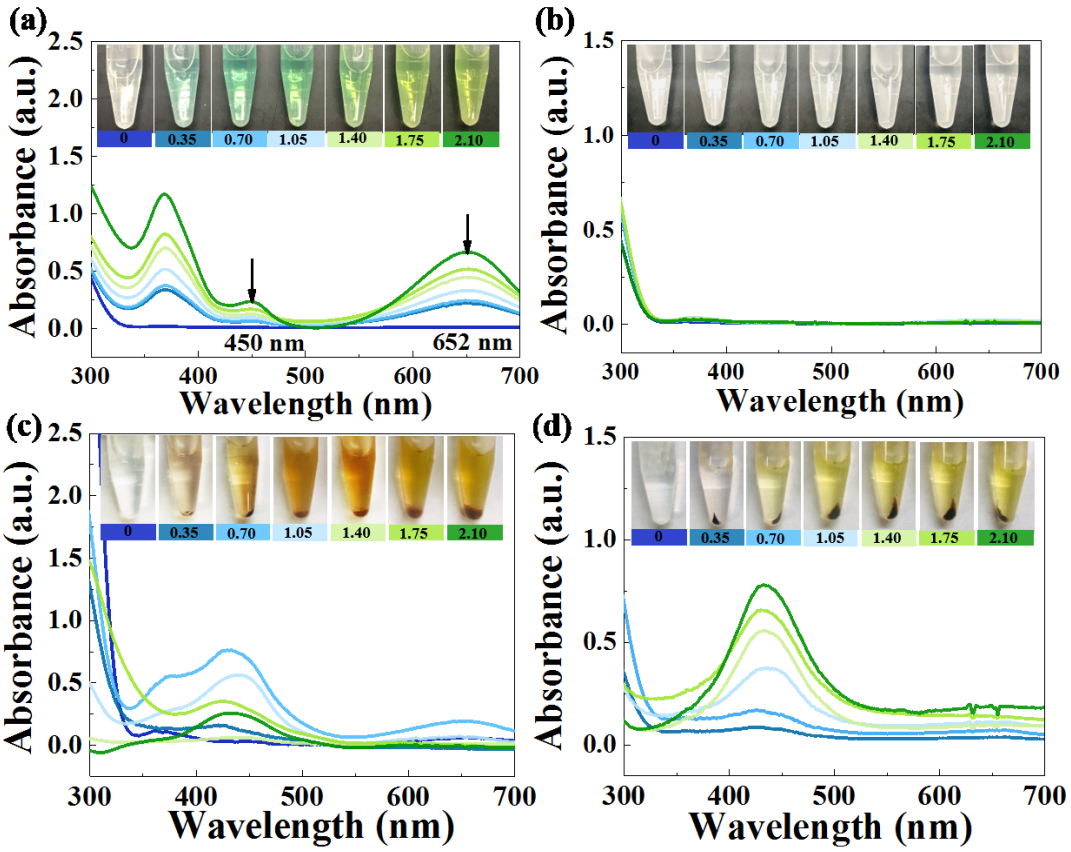

Figure S3. (a) UV-Vis spectra of TMB (0.5 mM) oxidation by bare CeO_2 for 12 h. (b) UV-Vis spectra of the supernatant after centrifugation and adding phosphate. (c) UV-Vis spectra of TMB (0.5 mM) oxidation by 5 mM F-/CeO_2 for 12 h. (d) UV-Vis of the supernatant after centrifugation and adding phosphate (500 mM, 15 μL). The concentration of CeO_2 are 0, 0.35, 0.70, 1.05, 1.40, 1.75, 2.1 μM respectively at pH 4 (acetate buffer, 25 mM).

Additional cyclic voltammetry data.

For $n\Delta E_p$ < 200 mV (E_p: peak potential), the direct electron transfer rate constant (K_s) for the CeO_2 NPs immobilized on the GCE was obtained by the following equation:[S1]

$$\text{Log } Ks = \alpha \log (1-\alpha) + (1-\alpha) \log \alpha - \log RT/nFv \qquad \text{(Eq. S1)}$$

where α is the charge transfer coefficient (0.5), n represents the number of electrons transferred (which is 1 in this case), v is the scan rate (50 mV s^{-1}), R is the gas constant, F is the Faraday's constant, while T is the temperature.

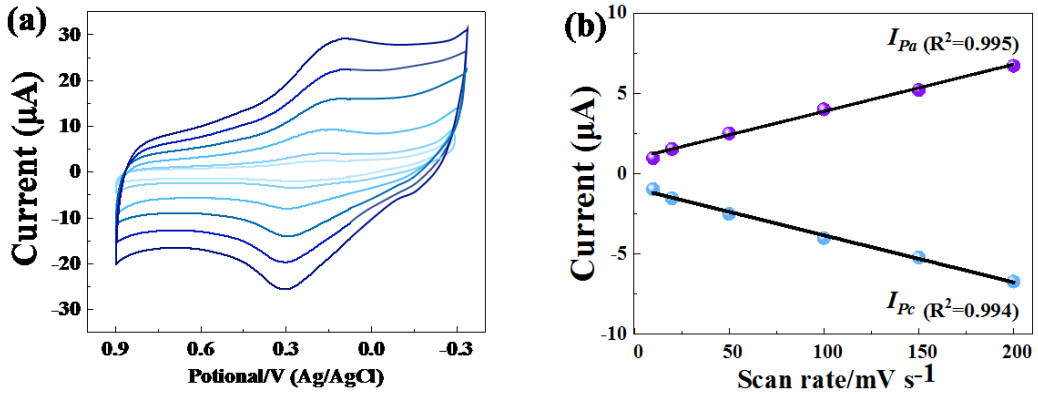

Figure S4. (a) The CV curves of the F^-/CeO_2 GCE in 500 mM acetate buffer (pH 4.0) at different scan rates. Scan rates (from inside out) were 10, 20, 50, 100, 150, 200 mV s^{-1}. (b) The anodic and cathodic peak current as function of scan rate. In all these measurements, dissolved oxygen in solution was removed by bubbling in nitrogen for 30 min.

Additional References

S1. E. Laviron, *J. Electroanal. Chem. Interfacial Electrochem.*, 1979, **101**, 19-28.