

## Electronic Supplementary Information

### **Intentional hydrolysis to overcome the hydrolysis problem: detection of Ce(IV) by producing oxidase-like nanozymes with F<sup>-</sup>**

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## Materials and Methods

### Chemicals

HNO<sub>3</sub>, HOAc, NaOH, NaF, NaCl, NaBr, EDTA-2Na, NaNO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, and Na<sub>2</sub>HPO<sub>4</sub> were from Mandel Scientific (Guelph, ON, Canada). N-(morpholino) ethanesulfonic acid (MES), 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), CeO<sub>2</sub> nanoparticles (catalogue number: 289744), Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and other metal ions were purchased from Sigma-Aldrich (St Louis, USA). Milli-Q water was used for all of the experiments.

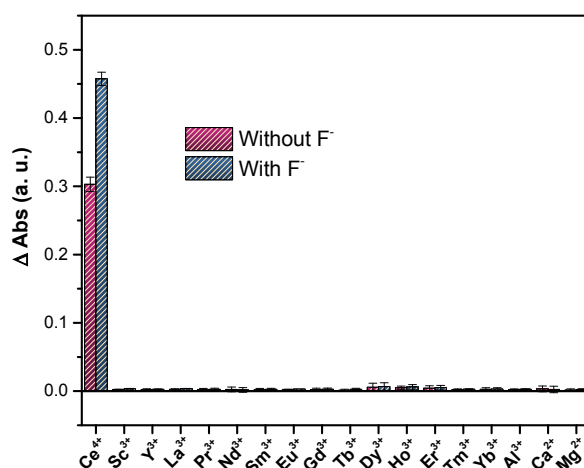
20 mM fresh Ce(IV) was prepared by dissolving Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> in Milli-Q water. Heated samples were prepared by heating 20 mM fresh Ce(IV) at 90 °C for 1, 3 and 6 h in a heat block (Fisher Scientific, model: Isotemp™ 2050FS 30 well block). The sample heated for 1 h is named Ce90<sub>1h</sub>. Working solutions were prepared by diluting the fresh or heated Ce(IV) with MilliQ-water. All the solutions were freshly prepared each time when they were to be used. The F<sup>-</sup> solution was prepared by dissolving NaF in Milli-Q water.

### Oxidation of ABTS

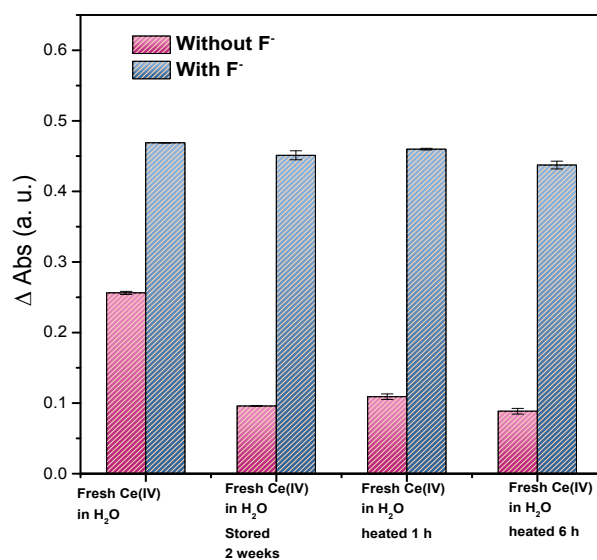
Typically, 10 μL of Ce(IV) solution, 10 μL F<sup>-</sup> solution, and 10 μL ABTS were successively added to 470 μL of acetate buffer (pH 4, 20 mM). After 15 min reaction, the resulting solutions were measure to get the UV-vis spectra using a spectrometer (Agilent 8453A). The ΔAbs (ΔAbs = A<sub>t</sub> - A<sub>0</sub>, where A<sub>t</sub> and A<sub>0</sub> are the absorbance at 415 nm of resulting solution in the presence and absence of Ce(IV) solution, respectively) was used to calculate ABTS oxidation. All the experiments were conducted at least in duplicate and the average values were reported. The concentration of F<sup>-</sup>, Ce(IV) and other metal ions, and the pH value were sometimes changed to investigate their effects.

### Kinetic measurements

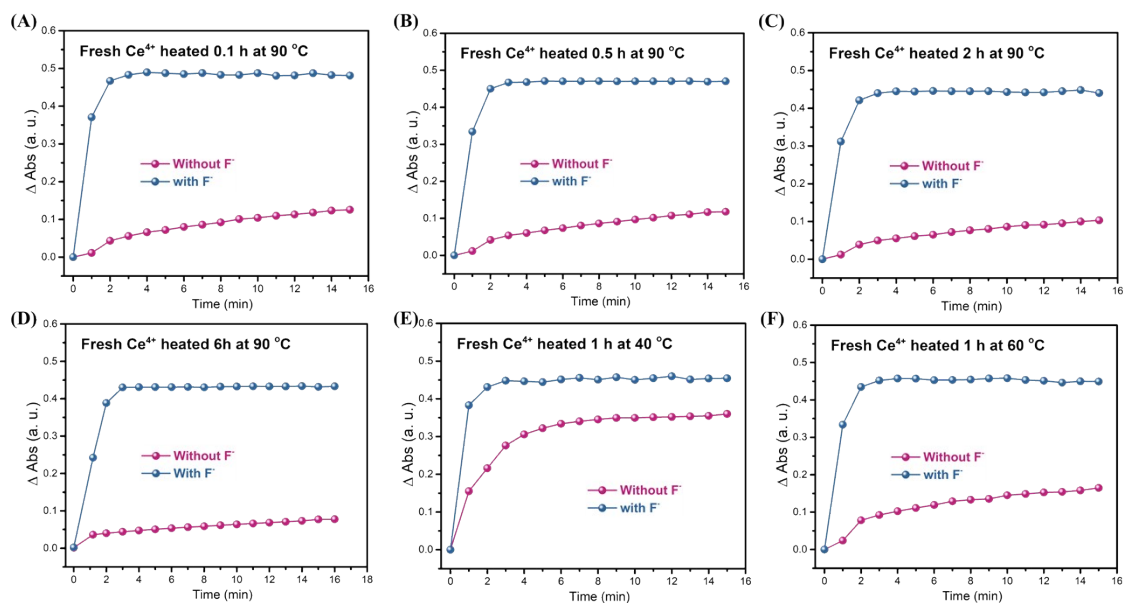
Typically, 10 μL of Ce(IV) solution (2.5 mM) and 10 μL F<sup>-</sup> solution (20 mM) were added to 470 μL of acetate buffer (pH 4, 20 mM). 10 μL of ABTS (10 mM) was introduced to initiate the reaction. The absorbance at 415 nm was monitored by using a microplate reader.



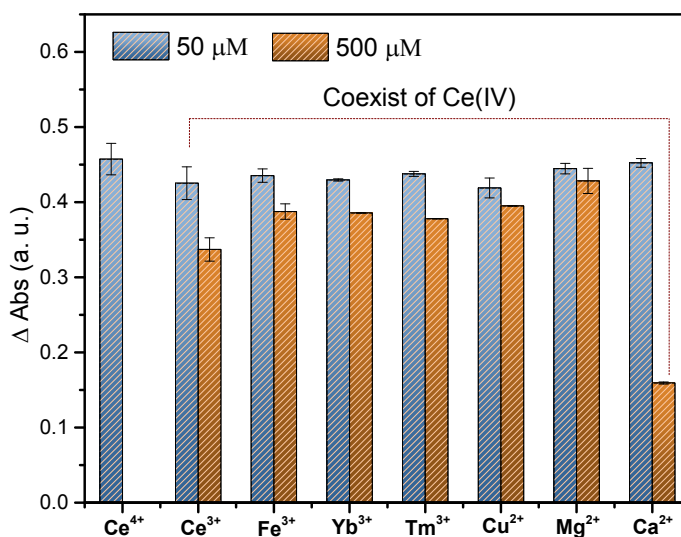
**Fig. S1.** Effect of various other metal ions (50  $\mu\text{M}$  each) on ABTS oxidation (monitored at 415 nm) without and with  $\text{F}^-$  (400  $\mu\text{M}$ ) in pH 4 acetate buffer (20 mM). The concentration of ABTS was 0.2 mM.



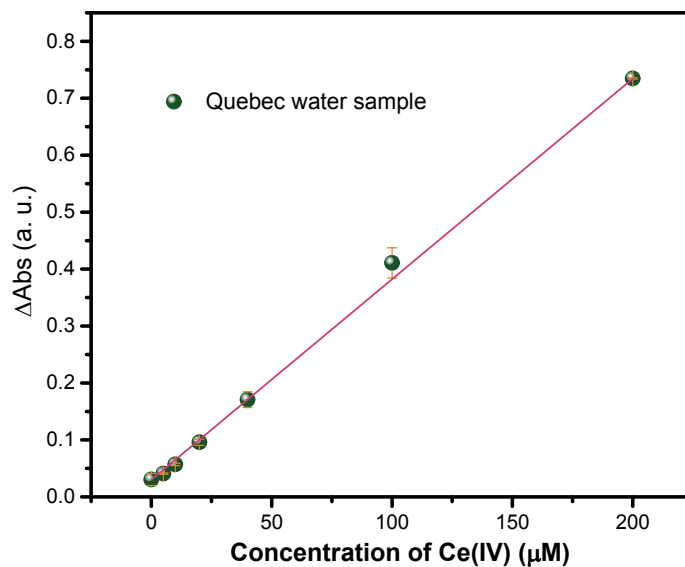
**Fig. S2.** Oxidation of 0.2 mM ABTS (monitored at 415 nm) by Ce(IV) (50  $\mu\text{M}$ ) after various thermal treatments without and with  $\text{F}^-$  (400  $\mu\text{M}$ ) in pH 4 acetate buffer (20 mM).



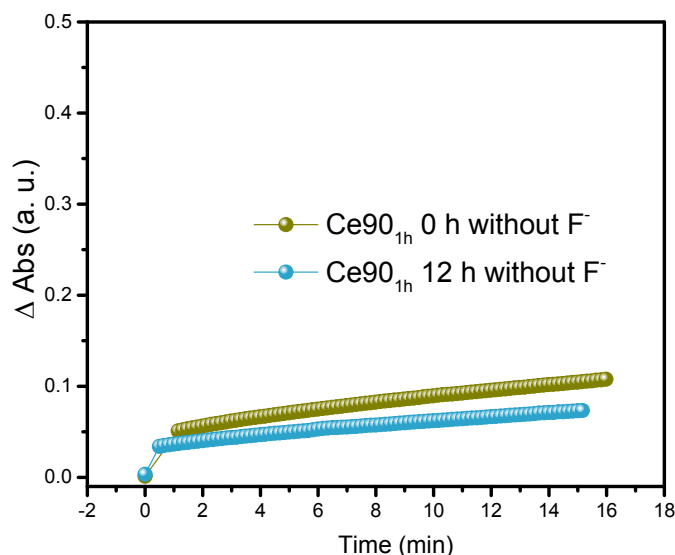
**Fig. S3.** Effect of  $F^-$  (0 or 400  $\mu M$ ) on the kinetics of 0.2 mM ABTS oxidation (monitored at 415 nm) in pH 4 acetate buffer (20 mM) in the presence of 50  $\mu M$  Ce(IV) heated at 90  $^{\circ}C$  for (A) 0.1 h, (B) 0.5 h, (C) 2 h and (D) 6 h, and heated at (E) 40  $^{\circ}C$  and (F) 60  $^{\circ}C$  for 1 h.



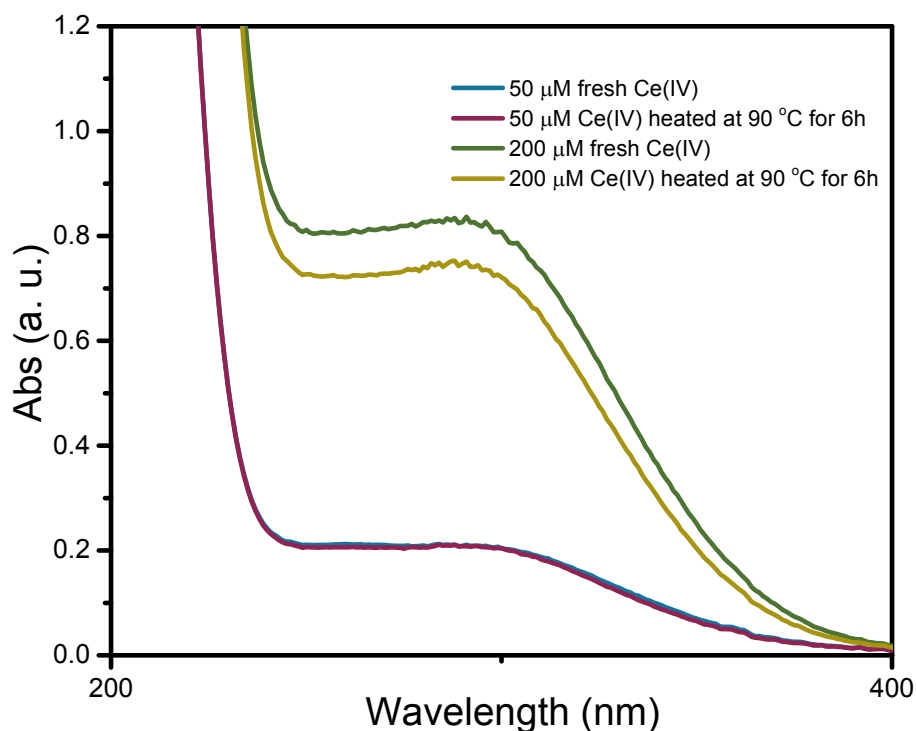
**Fig.S4.**  $Ce_{90_{1h}}$  (50  $\mu M$ ) and its mixtures with various metal ions (50 and 500  $\mu M$ ) on oxidation of ABTS (0.2 mM) in the presence of 400  $\mu M$   $F^-$ . All the metal ions mixtures were heated at 90  $^{\circ}C$  for 1 h and the ABTS oxidation was performed for 15 min in 20 mM acetate buffer, pH 4.



**Fig. S5.** Detection of Ce90<sub>1h</sub> on ABTS oxidation (415 nm) in a Quebec water sample at pH 4. The concentration of F<sup>-</sup> was 400 µM, and 0.2 mM ABTS was used. The pH of the water samples was adjusted by HNO<sub>3</sub>. The ABTS oxidation reaction was performed for 15 min. The regression equation is  $\Delta\text{Abs} = 0.0300 + 0.0035 [\text{Ce(IV)}] (\mu\text{M})$ ,  $r^2 = 0.9998$ . The limit of detection (LOD) was calculated to be 2.1 µM according to  $3\sigma/\text{slope}$  ( $\sigma$  = standard deviation of the blank signal).



**Fig. S6.** Kinetics of Ce90<sub>1h</sub> (50 µM) oxidation of ABTS (0.2 mM). The Ce90<sub>1h</sub> sample was incubated in the pH 4 acetate buffer in absence of F<sup>-</sup> for 0 or 12 h without F<sup>-</sup>.



**Fig. S7.** UV-vis absorbance spectra of various hydrolyzed samples after centrifugation to test the extent of hydrolysis.  $\text{Ce}^{4+}$  has a characteristic UV-Vis absorption peak at around 300 nm.<sup>1-3</sup> We heated freshly prepared Ce(IV) at 90 °C for 6 h, then centrifuged them at 15000 rpm for 20 min, and measured the UV-Vis spectra data of the supernatant. The peak intensity for 50  $\mu\text{M}$  Ce(IV) did not show obvious change. A higher concentration of Ce(IV) (200  $\mu\text{M}$ ) showed a slight decline on the intensity of the peak by  $\sim 10\%$ . Since we know that after this heating treatment, the samples were significantly hydrolyzed, the implication here is that the hydrolyzed products were not large aggregates or large particles, but likely to be loosely structured materials with a small density.

#### Additional references

1. A. Fawzy, I. I. Althagafi and H. M. Altass, *Int. J. Chem. Kinet.*, 2017, **49**, 143-156.
2. G. Lente and I. Fábián, *Inorg. Chem.*, 2004, **43**, 4019-4025.
3. A. Medalia and B. Byrne, *Anal. Chem.*, 1951, **23**, 453-456.