Electronic Supplementary Information

Boosting the oxidase mimicking activity of nanoceria by fluoride capping: rivaling protein enzymes and ultrasensitive F^- detection

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Table S1. Comparison of catalytic constant (k_{cat}) of nanoceria with natural enzymes.

Enzyme	Substrate	k_{cat} (s^{-1})	k_{cat}/K_m (mM^{-1} s^{-1})	Ref.
CeO_2	ABTS	2.80	15.56	This work
F-CeO_2	ABTS	12.84	207.10	This work
CeO_2	TMB	0.16	0.11	This work
F-CeO_2	TMB	1.47	10.47	This work
Glucose Oxidase	glucose	9.71	1.99	S1
l-Hydroxynicotine Oxidase	(S)-nicotine	0.033 ± 0.002	0.042 ± 0.007	S2
Choline Oxidase	choline	60 ± 1	237 ± 9	S3
Tyrosinase	quercetin	12.13	462.45	S4
5-Hydroxymethylfurfural Oxidase	vanillyl alcohol	21 ± 0.42	29	S5
Human Spermine Oxidase	spermine	6.6 ± 0.2	37 ± 7	S6
Phenylacetone Monooxygenase	NADPH	0.016	20	S7

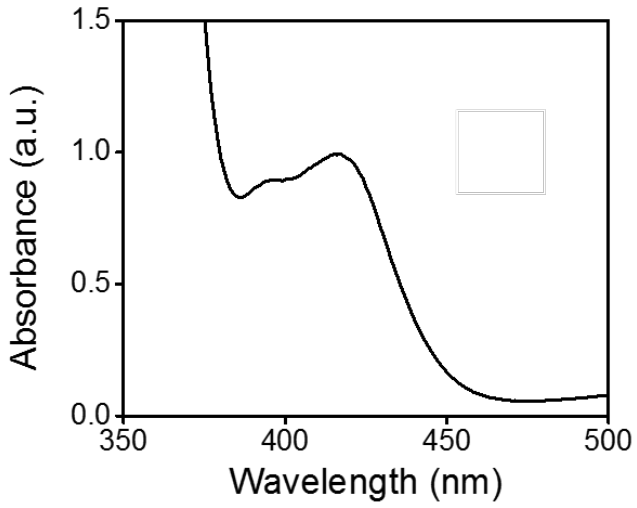

Figure S1. The UV-vis absorption spectrum of ABTS (2 mM) after incubating with nanoceria (50 μg/mL or 215 nM) overnight in a pH 4 acetate buffer (diluted 10 times for the measurement). The concentration of oxidized ABTS is calculated to be 0.26 ± 0.01 mM using the absorbance at 420 nm. ($\varepsilon = 3.6 \times 10^4$ M^{-1} cm^{-1}). Thus, the turnover number is 1200 ± 60 ABTS molecules for each nanoceria particle.

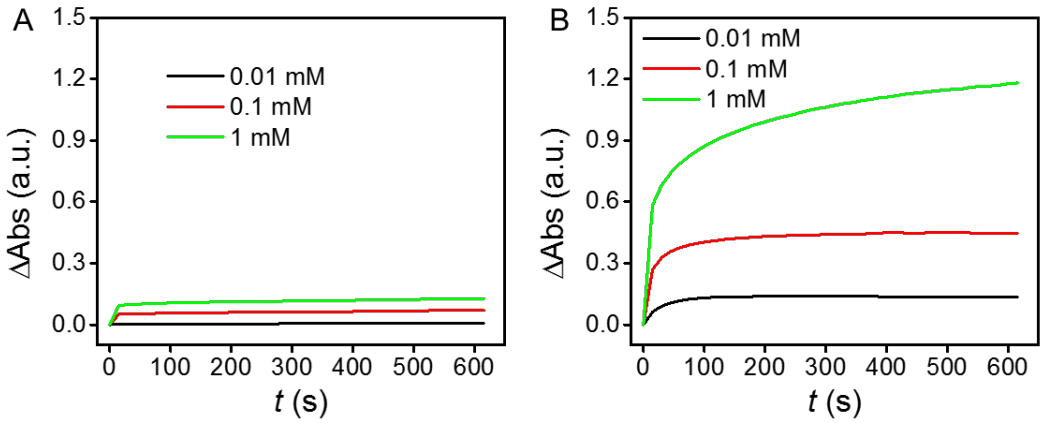

Figure S2. Kinetic traces of ABTS oxidation at different concentrations catalyzed by nanoceria (100 µg/mL) in the (A) absence and (B) presence of fluoride (0.5 mM). The reaction was performed at pH 4 (acetate buffer, 20 mM).

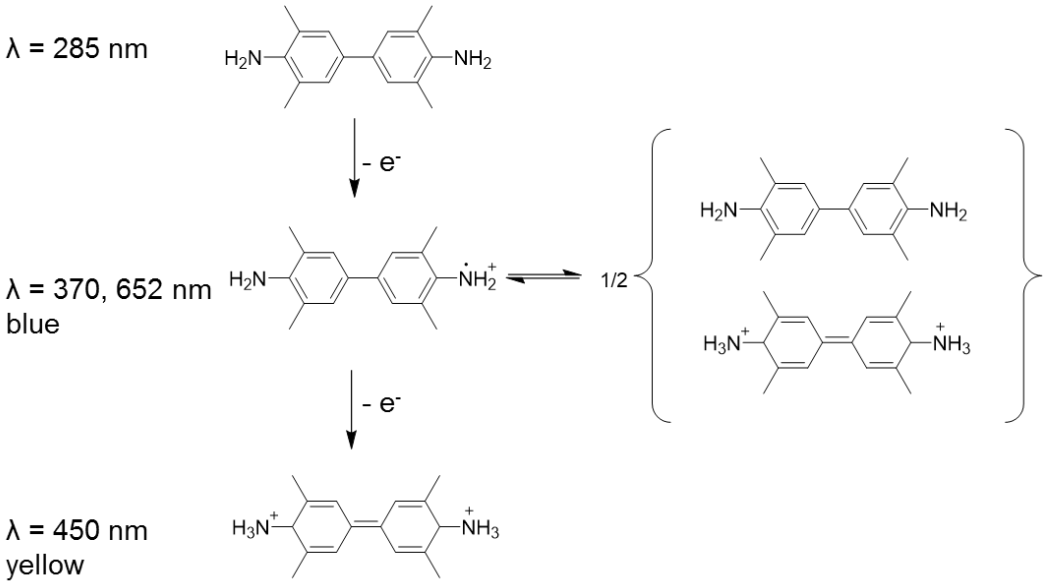

Figure S3. Reaction mechanism of TMB oxidation. TMB is positively charged at pH 4 with two amino groups. The non-oxidized TMB has an absorbance peak at 285 nm. One-electron product is a cationic free radical in equilibrium with its charge-transfer products, and the absorbance peaks are 370 nm, and 652 nm. The two-electron oxidation product is yellow with peak absorbance at 450 nm. [S8, S9]

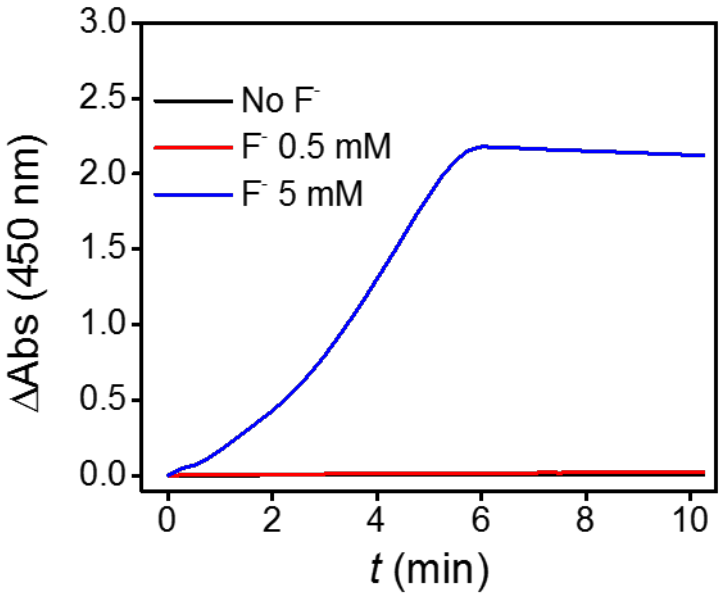

Figure S4. Kinetics of fluoride promoted oxidation of TMB (0.1 mM) catalyzed by nanoceria by monitoring the absorbance at 450 nm (two-electron product). The concentration of nanoceria was 100 µg/mL. The reaction was carried out in pH 4 acetate buffer (20 mM). After the initial dramatic increase, the absorbance at 652 nm decreased quickly to the background level within 5 min (Figure 3B of the main paper, blue trace). This activity decrease is due to the generation of two-electron product of TMB (Figure S3), which is confirmed by the yellow color of the reaction product (Figure 3B, inset), and the increase of absorbance at 450 nm.

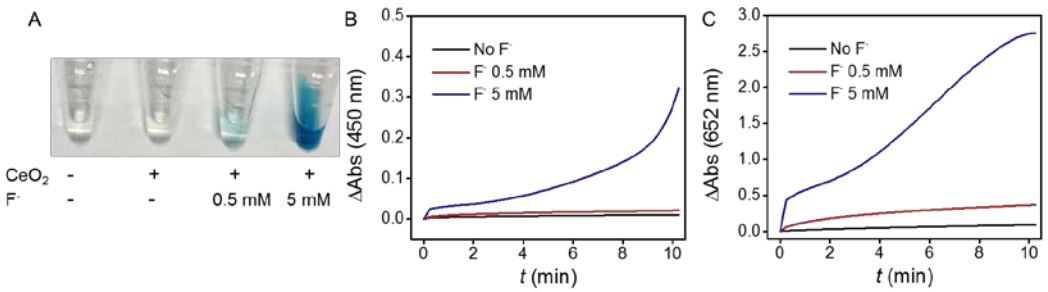

Figure S5. Photographs (A) and kinetic traces (B, C) of fluoride promoted oxidation of TMB (0.5 mM) catalyzed by nanoceria. The absorbance at 450 nm (two-electron product, B) and 652 nm (one-electron product, C) were respectively monitored. The concentration of nanoceria was 100 μg/mL. The reaction was carried out in pH 4 acetate buffer (20 mM).

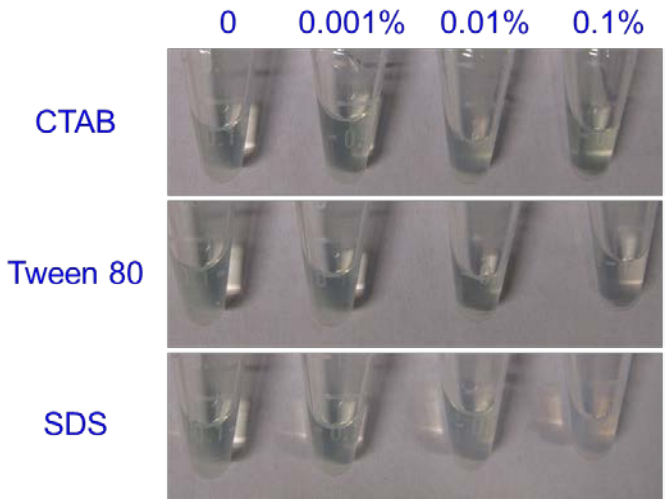

Figure S6. Effect of surfactants on the oxidase activity of nanoceria. Nanoceria (50 μg/mL) was incubated with surfactants (positively charged CTAB, neutral Tween 80, and negatively charged SDS) of different concentrations for 2 h before adding ABTS (1 mM). No fluoride was added in these samples. The images were taken after 15 min reaction. No enhanced reaction was observed for any of all the three surfactants. The adsorbed surfactant layers on nanoceria may block the direct interaction between the substrate and nanoceria.

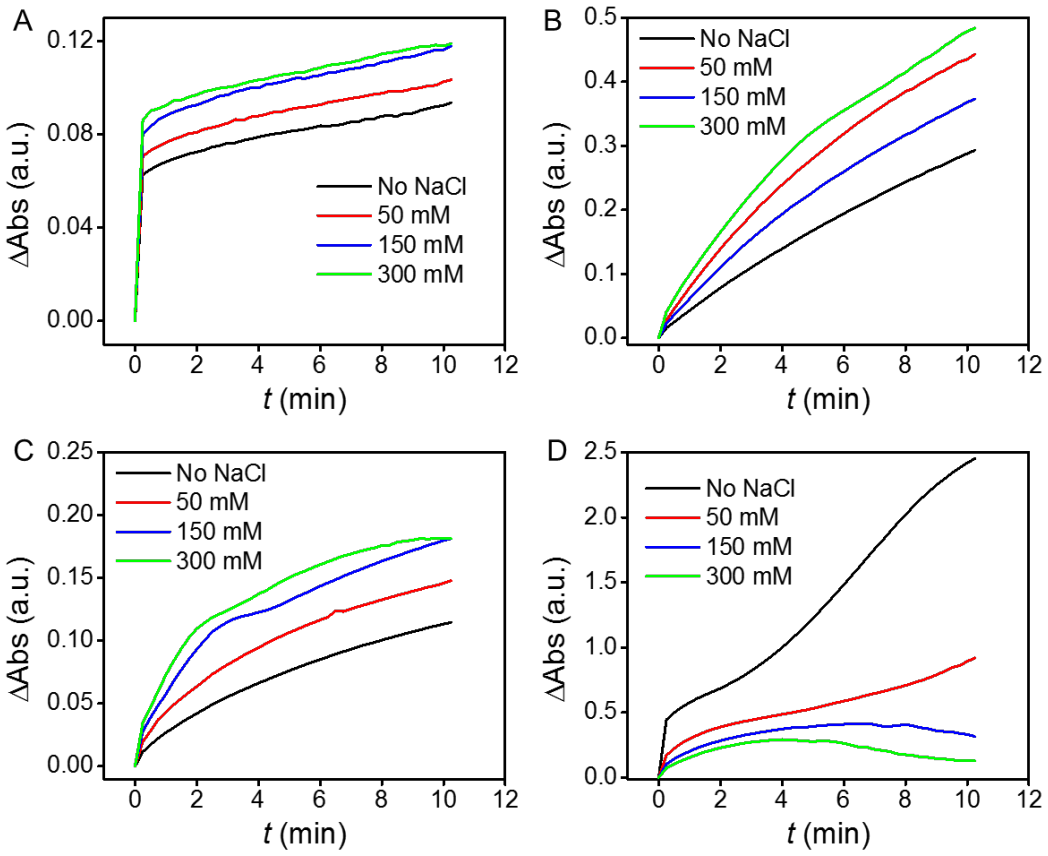

Figure S7. The effect of NaCl concentration on the oxidation of (A,B) ABTS and (C,D) TMB catalyzed by nanoceria (100 μg/mL) in the (A,C) absence or (B,D) presence of 5 mM F^-, respectively. The reaction was carried out in a pH 4 acetate buffer (20 mM). The absorbance at 420 nm for ABTS and at 652 nm for TMB was monitored. For the negatively charged ABTS, increasing the NaCl concentration did not affect the initial oxidation of ABTS in the absence of F^-, With 5 mM F^-, NaCl has a positive role when the surface is negative with a saturated fluoride layer. On the other hand, for positively charged TMB, the initial reaction rate was increased for bare nanoceria (cationic surface), but decreased for the F^--capped nanoceria (anionic surface). With F^- modification, nanoceria is negatively charged, repelling the negatively charged ABTS and attracting the positively charged TMB.

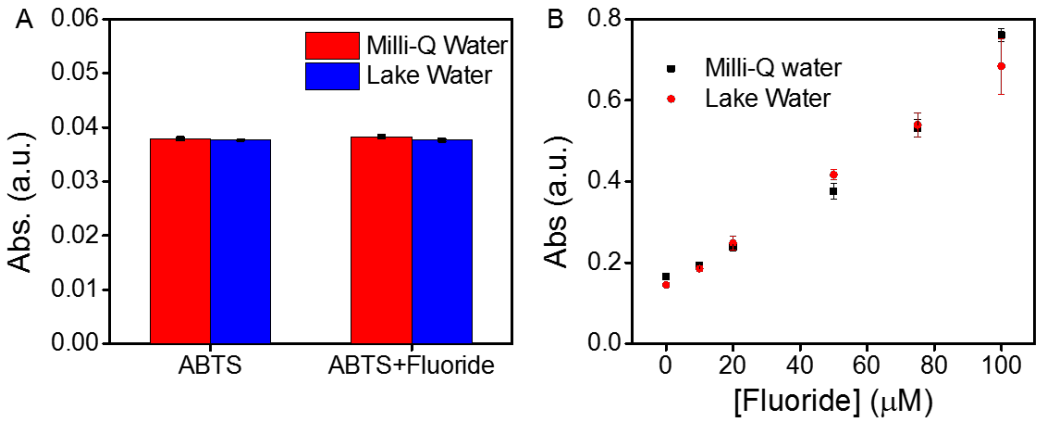

Figure S8. Detection of fluoride in Lake Huron water. A) Effect of Lake Huron water on ABTS oxidation. ABTS (0.5 mM) was incubated in pH 4 acetate buffer (20 mM) in Milli-Q water or Lake Huron water. The absorbance at 420 nm was recorded after 10 min. Fluoride (1 mM) was added into both water samples. B) Comparison of fluoride detection in Milli-Q water and Lake Huron water. Error bars represent the standard deviation from three individual measurements.

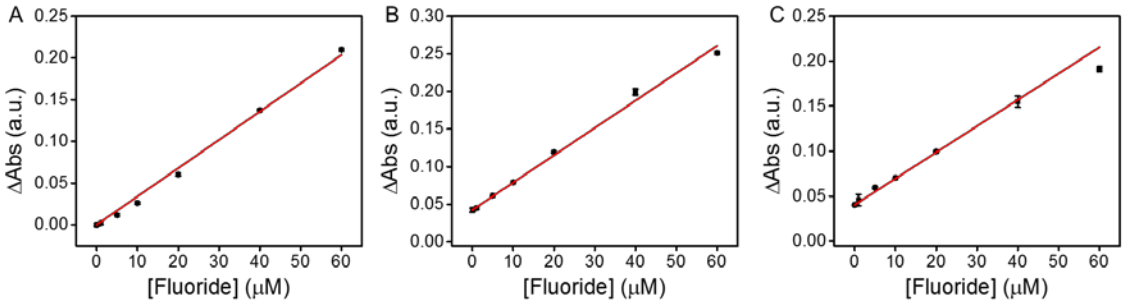

Figure S9. Detection of fluoride in toothpastes using the standard addition method by adding various concentrations of NaF: (A) a fluoride-free toothpaste, (B) a normal toothpaste (0.254%), and (C) a high fluoride toothpaste (1.1%). Each toothpaste was dispersed and diluted in Milli-Q water. The final assays contained ABTS (0.5 mM), nanoceria (20 μg/mL), and spiked fluoride (from 0 to 60 μM). The reaction was carried out in the acetate buffer (pH 4, 20 mM). The error bars represent standard deviation from three individual measurements.

Additional References

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