

## Supporting Information

### **Synergistically Boosted Degradation of Organic Dyes by CeO<sub>2</sub> Nanoparticles with Fluoride at low pH**

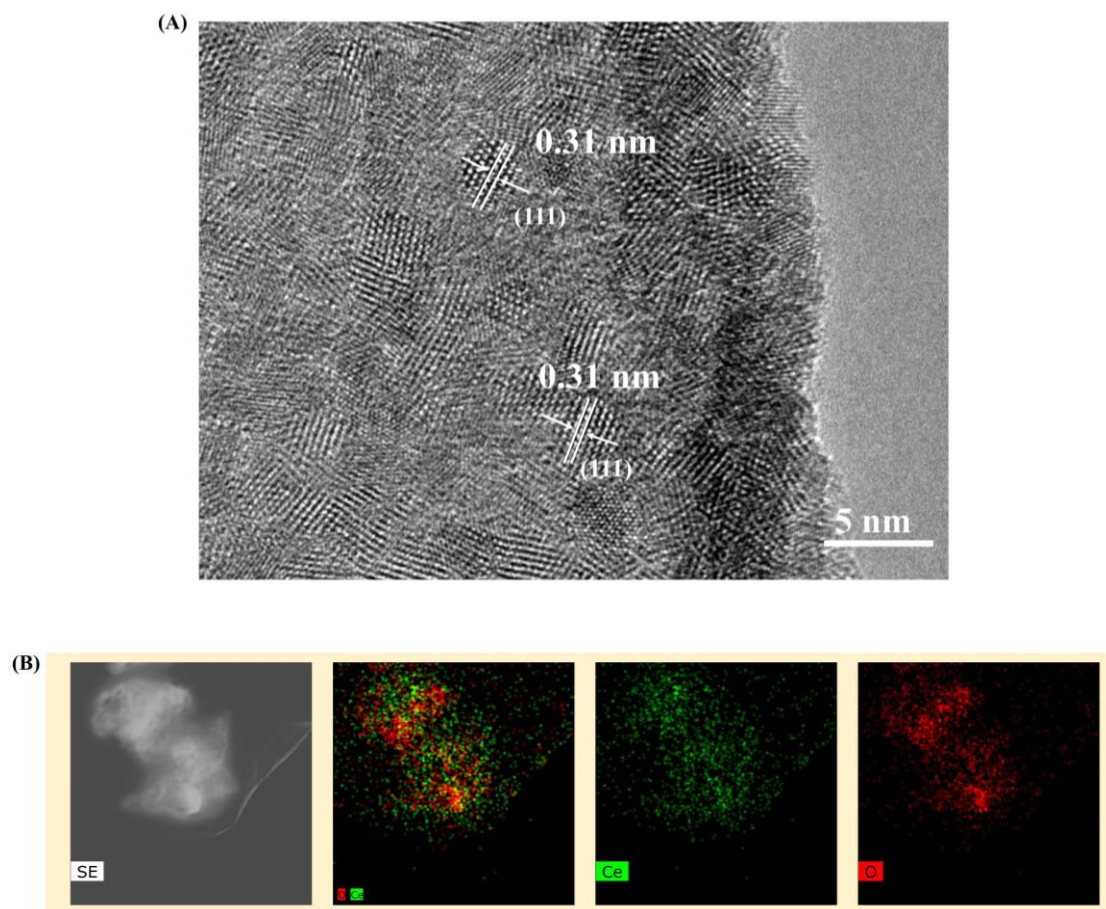
Yawen Wang<sup>1,2\*</sup>, Tongtong Liu<sup>1</sup> and Juewen Liu<sup>2\*</sup>

*1. College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China.*

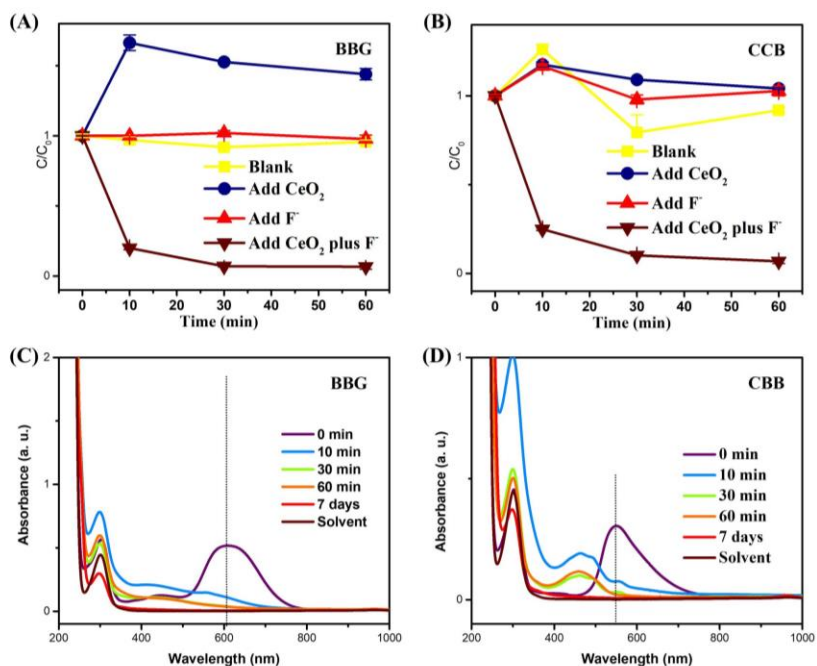
*Email: wangyawen@tyut.edu.cn*

*2. Department of Chemistry, Waterloo Institute for Nanotechnology, Water Institute, University of Waterloo, Ontario, N2L 3G1, Canada*

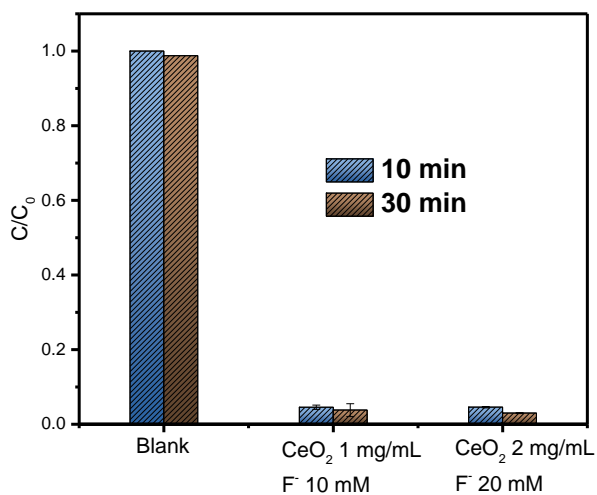
*Email: liujw@uwaterloo.ca*



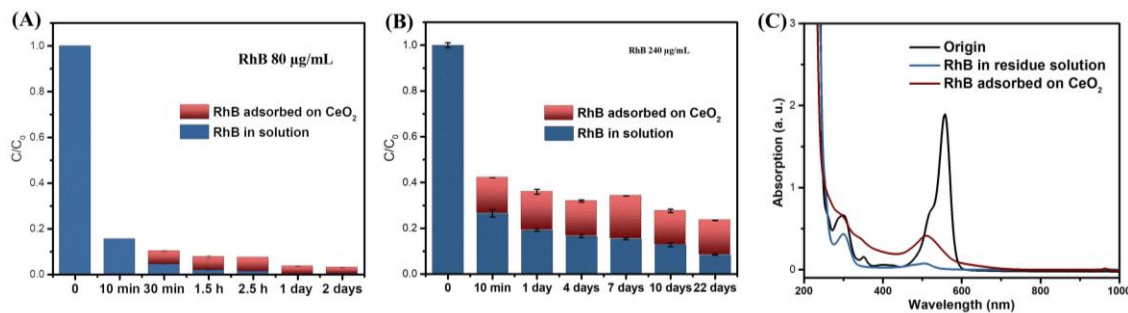
**Figure S1.** (A) A high resolution TEM micrograph, and (B) EDX element mapping of the  $\text{CeO}_2$  nanoparticles used in this work.



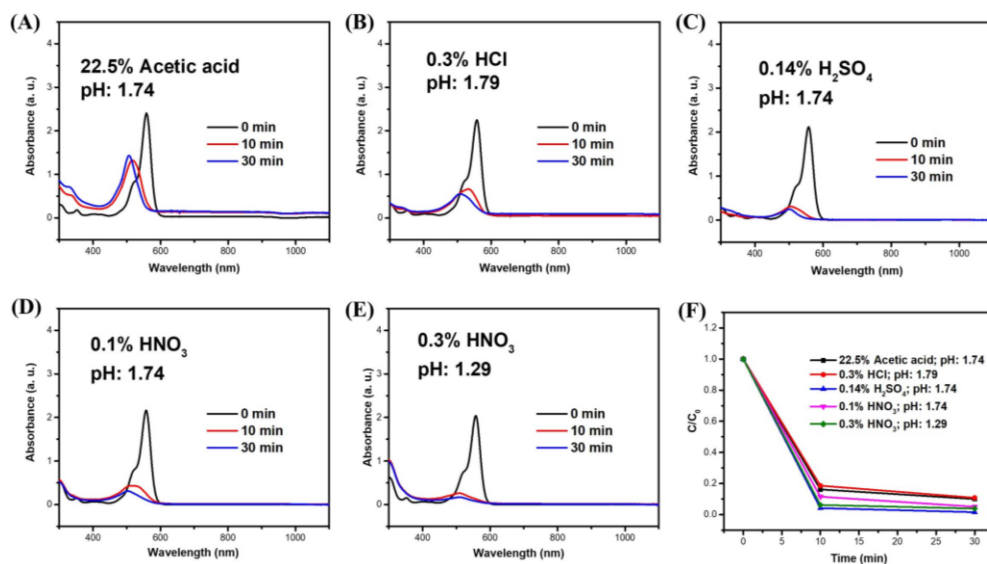
**Figure S2.** Kinetics of degradation of (A) BBG; and (B) CBB with  $CeO_2$  under different conditions at pH 1.29. UV-vis spectra of (C) BBG; and (D) CBB with  $CeO_2$  plus  $F^-$  at pH 1.29 with time. Concentration of dyes: 10  $\mu\text{g/mL}$  each; concentration of  $CeO_2$ : 0.2  $\text{mg/mL}$ ; concentration of  $F^-$ : 2  $\text{mM}$ .



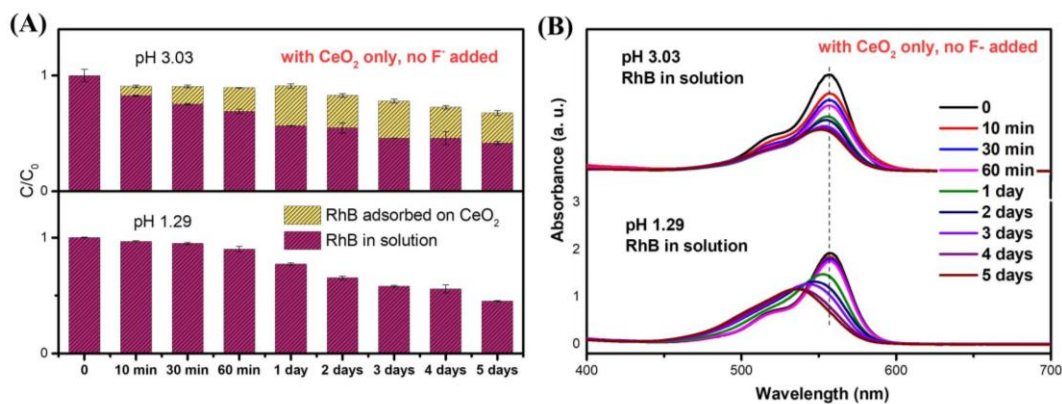
**Figure S3.** Effect of  $CeO_2$  and  $F^-$  concentration on the degradation of 10  $\mu\text{g/mL}$  RhB at pH 1.29



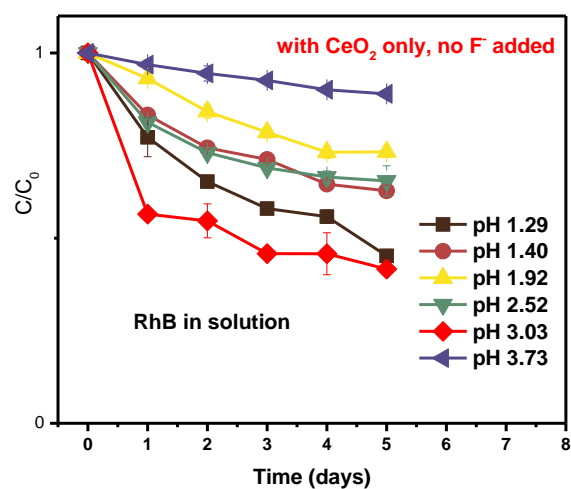
**Figure S4.** Dye degradation efficiency by  $CeO_2$  (0.2 mg/mL) plus  $F^-$  (2 mM) at pH 1.29 in the presence of (A) 80  $\mu\text{g/mL}$  and (B) 240  $\mu\text{g/mL}$  RhB. (C) UV-vis absorption spectra of RhB (80  $\mu\text{g/mL}$  each) in solution and adsorbed on  $CeO_2$  (0.2 mg/mL) after aged for 1 day with  $F^-$  (2 mM). Although  $CeO_2$  adsorbed some degraded products, this was not the main reason of decoloration. A significant amount of degradation occurred. The original RhB peak not only decreased, but also shifted. With 3-fold more RhB added, the fraction of decoloration decreased, although the absolute amount of decolored RhB was higher. The amount of RhB adsorbed on  $CeO_2$  was calculated by the following method. After the reaction, the samples were centrifuged and the precipitate was treated twice with NaOH (1 mL, 1 M) and ultrasonic at 40  $^{\circ}\text{C}$  for 1 h. The RhB can be washed out by NaOH. Then the concentration of RhB in NaOH at each time pointed was measured by UV-vis spectrometry. Accordingly, the amount of RhB adsorbed on  $CeO_2$  could be obtained.



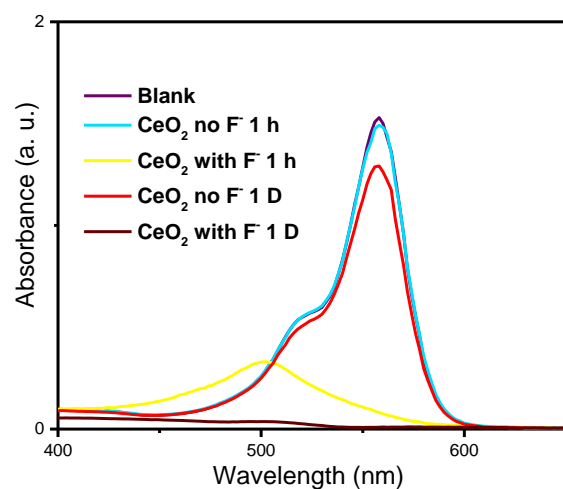
**Figure S5.** Effect of different types of acids on RhB degradation performance: (A) acetic acid; (B) HCl; (C) H<sub>2</sub>SO<sub>4</sub>; (D) 0.1% HNO<sub>3</sub>; and (E) 0.3% HNO<sub>3</sub>. (F) A comparison of the degradation kinetics. Concentration of CeO<sub>2</sub>: 0.2 mg/mL; concentration of F<sup>-</sup>: 2 mM; concentration of RhB: 10 µg/mL



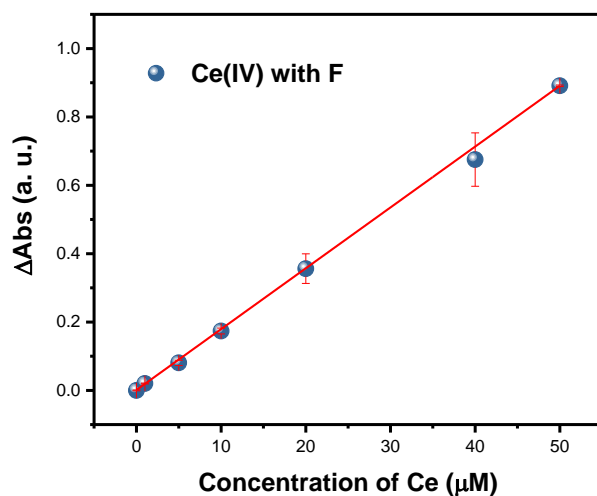
**Figure S6.** (A) degradation efficiency by CeO<sub>2</sub>; and (B) the UV-Vis spectra of RhB of the samples at pH 3.03 and 1.29 in the absence of F<sup>-</sup>. Concentration of RhB: 10 µg/mL; no fluoride added here. At pH 3.03, we mainly observed adsorption without much peak shift, while at pH 1.29, we observed more degradation. Overall, the efficiency was much lower without F<sup>-</sup>.



**Figure S7.** Kinetics of RhB (10  $\mu\text{g/mL}$ ) degradation by  $\text{CeO}_2$  (0.2 mg/mL) at different pH values in the absence of  $\text{F}^-$ .

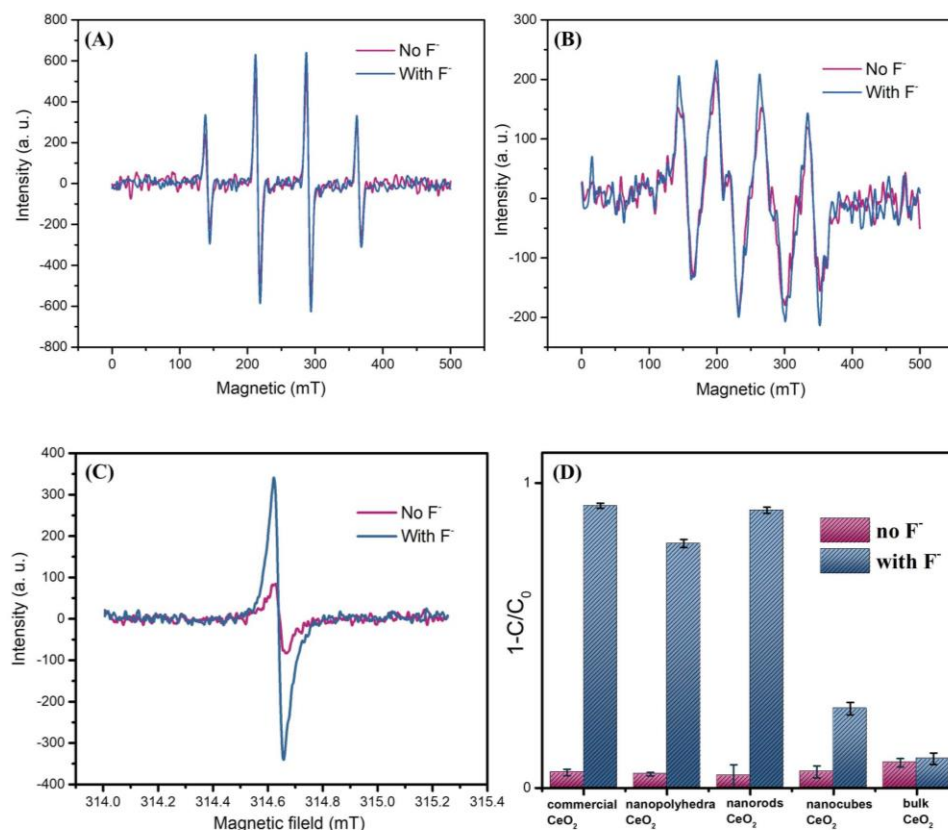


**Figure S8.** UV-vis absorption spectra of 10  $\mu\text{g/mL}$  RhB incubated with 0.2 mg/mL  $\text{CeO}_2$  nanorods at different conditions at pH 1.29 for 1 h or 1 day. Concentration of  $\text{F}^-$ : 0 or 2 mM.



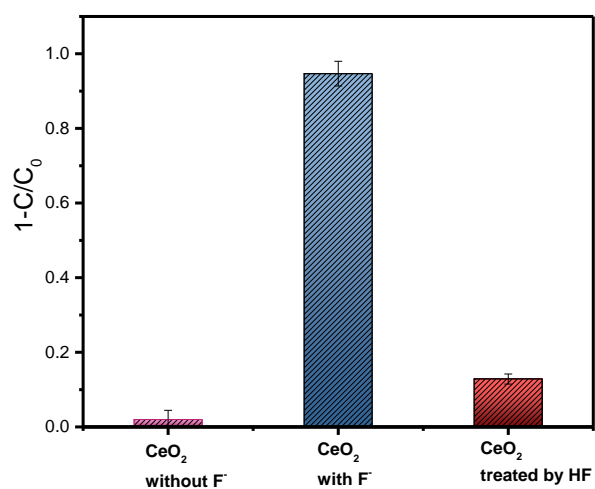
**Figure S9.** Effect of  $\text{Ce}^{4+}$  (prepared by dissolving  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  in Milli-Q water) concentration on 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) (0.2 mM) oxidation monitored at 415 nm within 15 min in the presence of 400  $\mu\text{M}$   $\text{F}^-$ . The regression equation is  $Y = 0.0178X + 0.0019$ ,  $r^2 = 0.999$ .

The test procedure was as follows: pH 1.29  $\text{HNO}_3$  containing the  $\text{CeO}_2$  nanorods (0.2 mg/mL) was respectively soaked without and with  $\text{F}^-$  (2 mM) for 1 h. We then centrifuged the solutions for 10 min to precipitate the  $\text{CeO}_2$ . The supernatant was collected for testing. Typically, 10  $\mu\text{L}$  of the prepared  $\text{Ce}^{4+}$  solution or supernatant from soaking of  $\text{CeO}_2$ , 10  $\mu\text{L}$   $\text{F}^-$  solution, and 10  $\mu\text{L}$  ABTS were successively added to 470  $\mu\text{L}$  of acetate buffer (pH 4, 20 mM). After 15 min reaction, the resulting solutions were measured to get the UV-vis spectra using a spectrometer (Agilent 8453A). The  $\Delta\text{Abs}$  ( $\Delta\text{Abs} = A_t - A_0$ , where  $A_t$  and  $A_0$  are the absorbance at 415 nm of the resulting solution in the presence and absence of  $\text{Ce}^{4+}$  solution, respectively) was used to calculate the oxidation of ABTS. All the experiments were conducted at least in duplicate and the average values were reported. The obtained average  $\Delta\text{Abs}$  for the supernatant in absence of  $\text{F}^-$  was 0.002, while in the presence of  $\text{F}^-$  was 0.081.

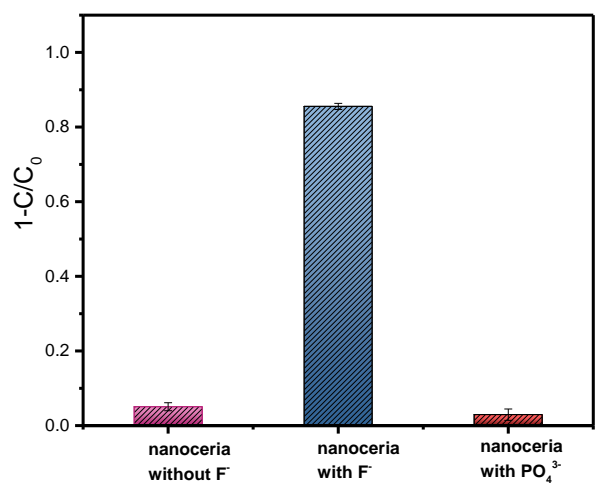


**Figure S10.** ESR spectra of radical adducts trapped by (A) DMPO-•OH; (B) DMPO-•O<sub>2</sub><sup>-</sup> in the CeO<sub>2</sub> nanoparticle dispersion (pH 1.29). (C) EPR spectra of CeO<sub>2</sub> nanoparticles without and with 2 mM F<sup>-</sup> in pH 1.29 solution. (D) Quantification of the decrease of the UV-vis spectra absorption peaks of RhB (10 μg/mL) for different CeO<sub>2</sub> (0.2 mg/mL) after 1 h. Concentration of F<sup>-</sup>: 2 mM. Three kind of nanoscale CeO<sub>2</sub> (nanopolyhedra in the size of 11.5±1.8 nm, nanorods with a uniform diameter in 9.6±1.2 nm and a less-uniform length within 50-200 nm and nanocubes in size of 36.1±7.1 nm) and one large size bulk CeO<sub>2</sub> were prepared according to the literature.<sup>1</sup> The results indicated in presence of F<sup>-</sup>, the bulk CeO<sub>2</sub> had no activity to degrade RhB. All nanoscale CeO<sub>2</sub> had the enhanced effect, but the degree of enhancement was different.





**Figure S11:** Quantification of the decrease of the UV-vis absorption peaks of RhB (10 µg/mL) for CeO<sub>2</sub> nanorods (0.2 mg/mL) at different conditions after 1 h. Concentration of F<sup>-</sup>: 2 mM.



**Figure S12:** Quantification of the decrease of the UV-vis absorption peaks of RhB (10 µg/mL) for nanoceria (0.2 mg/mL) at different conditions after 1 h. The concentrations of F<sup>-</sup> and PO<sub>4</sub><sup>3-</sup> were both 2 mM.

### **Preparation of CeO<sub>2</sub> nanomaterials.**

The nanoscale CeO<sub>2</sub> and bulk CeO<sub>2</sub> samples were prepared by the method of Mai et al.<sup>1</sup> For the nanoscale CeO<sub>2</sub>, 0.868 g of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and NaOH were dissolved in 40 mL of deionized water, and kept stirring for 30 min with the formation of a milky slurry. Then the slurry was transferred to Teflon-lined autoclave to hydrothermal treatment. The concentration of NaOH and hydrothermal temperature for fabricating nanopolyhedra, nanorods and nanocubes were 0.01 M (100°C), 6 M (100°C) and 6 M (180 °C), respectively. After the hydrothermal treatment, fresh white precipitates were separated by centrifugation, washed with deionized water and ethanol several times, followed by drying at 60 °C in air overnight. The bulk CeO<sub>2</sub> powder was prepared by the precipitation route at pH 11 at room temperature, using 0.868 g of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and NH<sub>4</sub>OH as the starting materials, followed by separation, washing, drying, and calcining at 650 °C for 4 h.

### **Analytical methods.**

Room temperature electron spin resonant (ESR) and low-temperature electron paramagnetic resonance (EPR) spectra were recorded on a Bruker model JES-FA200 spectroscopy. Samples were prepared by dispersing CeO<sub>2</sub> (0.2 mg/mL) nanoparticles with or without NaF (2 mM) in pH 1.29 testing solution. 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) was used as the spin trap. HNO<sub>3</sub> was used to adjust the pH of the solution.

### **Additional references**

1. Mai, H. X.; Sun, L. D.; Zhang, Y. W.; Si, R.; Feng, W.; Zhang, H. P.; Liu, H. C.; Yan, C. H., Shape-Selective Synthesis and Oxygen Storage Behavior of Ceria Nanopolyhedra, Nanorods, and Nanocubes. *J. Phys. Chem. B* **2005**, *109* (51), 24380-24385.