

Experimental Section

Reagents and Materials. Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and ammonium hydroxide (25–28 wt%, $\text{NH}_3 \cdot \text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Dextran T-10, 2-nitrobenzaldehyde, 2,2'-Azinobis-(3-ethylbenzthiazoline-6-sulphonate) (ABTS, diammonium salt) and 3,3',5,5'-Tetramethylbenzidine (TMB) were purchased from Sigma-Aldrich. H_2O_2 (30%), Sodium dihydrogen phosphate, disodium hydrogen phosphate, citric acid and sodium citrate were purchased from Beijing Chemicals (Beijing, China). All other reagents were of analytical reagent grade and used as received. Ultrapure water (18.2 M Ω ; Millipore Co., USA) was used throughout the experiment.

Measurements and Characterizations. Transmission electron microscope images (TEM) were recorded by a TECNAI F30 HRTEM high resolution TEM operated at 200 kV. The crystalline structure of the as prepared cerium oxide nanoparticles was characterized by Bruker AXS D8 advance X-ray diffractometer with Cu-K α radiation. The operating voltage and current were kept at 40 kV and 40 mA, respectively. The pH measurements were performed with a PB-10 portable pH meter (Sartorius Scientific Instruments (Beijing) Co., Ltd, China).

Preparation of Dextran-Coated Cerium Oxide Nanoparticles. Dextran-coated cerium oxide nanoparticles were prepared according to the literature

previously reported with a little modification.¹ In brief, 2.17 g cerium (III) nitrate was first dispersed in 5.0 mL of pure water, followed by the addition of 10.0 mL of 1.8 g dextran T-10. Then 30.0 mL ammonium hydroxide solution (25%-28%) was slowly added to the mixed solution by dropwise and stirred for 24 h at 25 °C. The color of the mixed solution changed from light yellow to dark brown, which indicated the formation of stabilized and well-dispersed dextran-coated ceria nanoparticles. Subsequently, in order to remove any debris as well as large agglomerates, the prepared mixed solution was centrifuged at 4000 rpm at least for two 30 min cycles. Moreover, the resultant suspension was centrifuged at 11000 rpm for 30 min. Finally, the obtained precipitate was washed with distilled water for three times, then stored at 4 °C.

Oxidase-Like Activity Evaluation. Nanoceria possesses a specific pH-dependent oxidase-like activity, which can rapidly oxidize a variety of organic substrates acidic pH values, without the help of any oxidizing agent. This oxidase-like activity of cerium oxide nanoparticles was evaluated by measuring the oxidation products oxTMB and ABTS⁺ with a UV/VIS/NIR Spectrometer (Lambda 750, Perkin Elmer). Typically, experiments were carried out using 0.1 mg/mL cerium oxide nanoparticles in a reaction volume of 800 µL buffer solution at pH 7.0 (or 4.0) with 1 mM TMB (or ABTS) as a substrate, unless otherwise stated.

Photochemical Control of Oxidase-Like Activity. The photo-mediated oxidase-like activity of dextran-decorated cerium oxide nanoparticles was performed in the phosphate buffer solution (0.5 mM, initial pH 7.0). Typically, 2-NBA/CeO₂ hybrid system was irradiated with a UV-lamp of 1.5 mW/cm² (Spectronics, America, SB-100P/FA, at 365 nm) for 10 min at room temperature. After UV irradiation, 1 mM TMB (or ABTS) was added to above mixture. And then, absorption spectra of reaction solutions by nanoceria were recorded by a UV/VIS Spectrometer (Lambda 750, PerkinElmer).

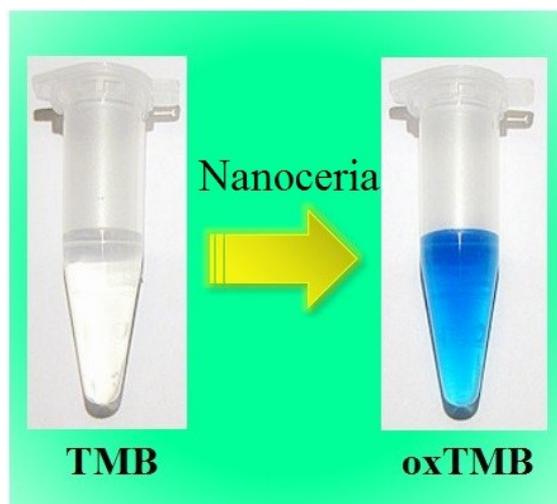


Figure S1. Visual color changes as a result of the catalyzed oxidation of TMB by nanoceria. [Nanoceria] = 0.1 mg/mL, [TMB] = 1 mM, [pH] =4.0.

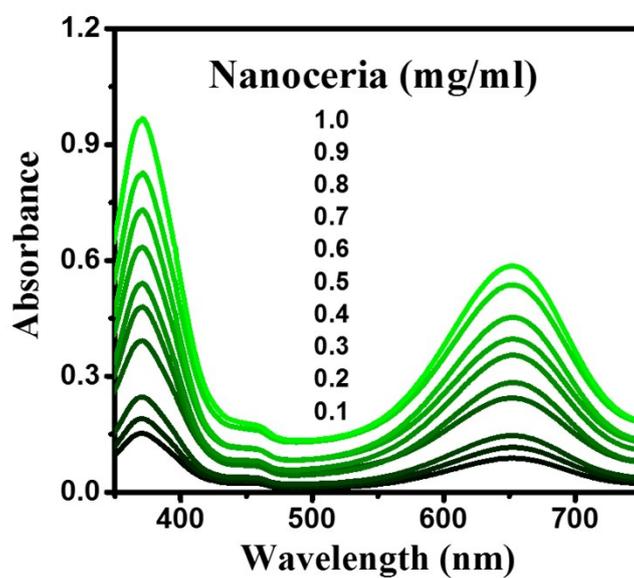


Figure S2. Absorption spectra and of TMB reaction solutions under different concentrations of cerium oxide nanoparticles.

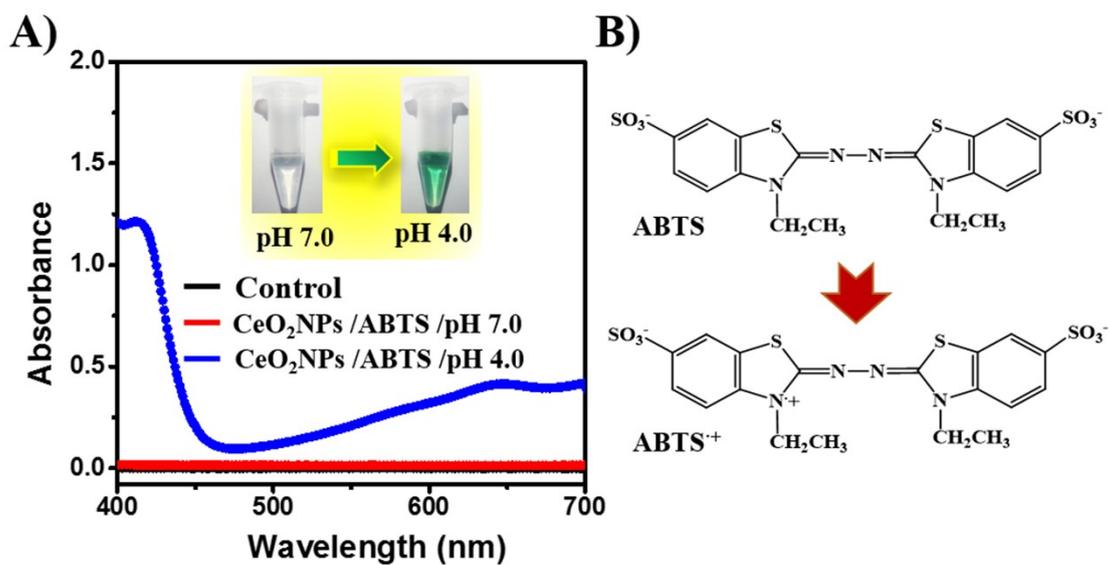


Figure S3. (A) Absorption spectra and of ABTS reaction solutions under different conditions. Inset: Photographs of ABTS/nanoceria solutions under different pH. (B) The molecular structures of ABTS and its oxidation product ABTS^{•+}.

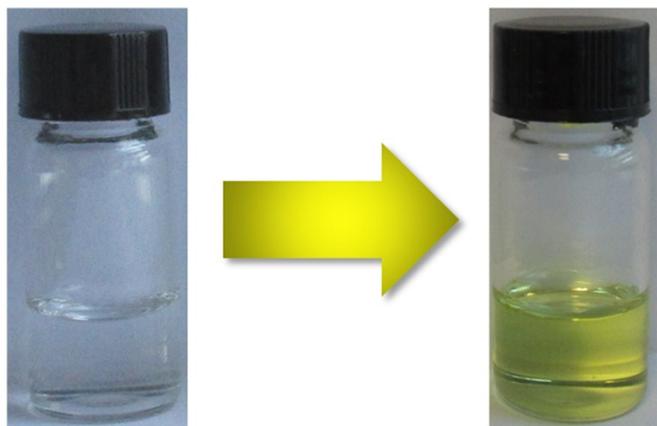


Figure S4. Photographs of an aqueous 2-NBA solution before and after irradiation with UV-lamp.

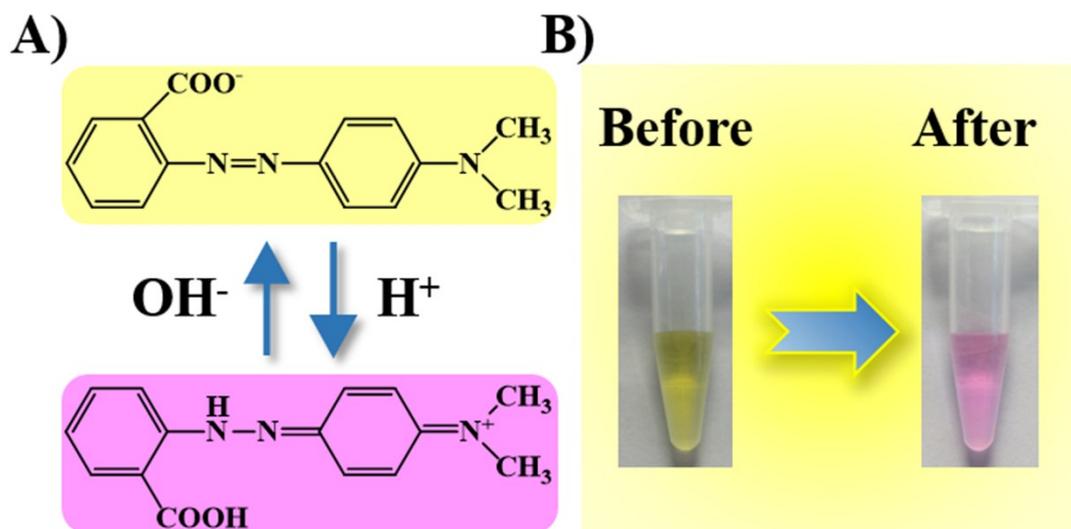


Figure S5. (A) Acid and base forms of methyl red; (B) The color change of 2-NBA/methyl red in the phosphate buffer solution (0.5 mM, initial pH 7.0) before and after light irradiation.

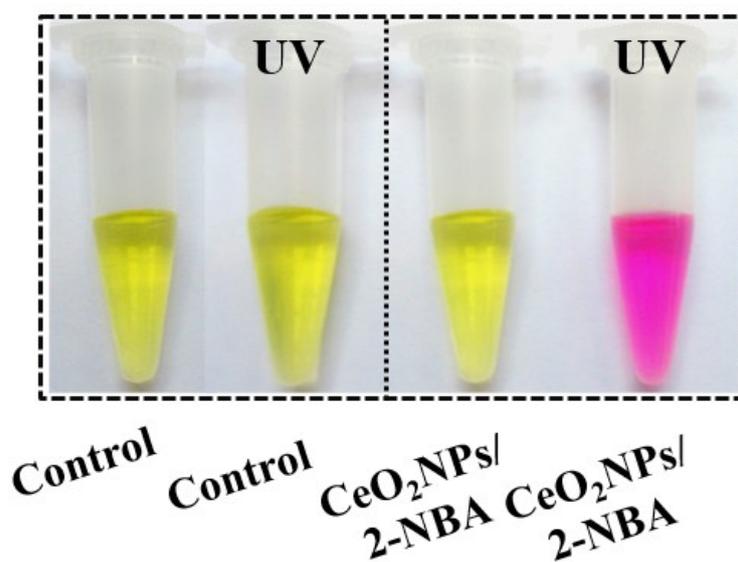


Figure S6. The color changes of methyl red alone and 2-NBA/methyl red/nanoceria in the phosphate buffer solution (0.5 mM, initial pH 7.0) before and after light irradiation.

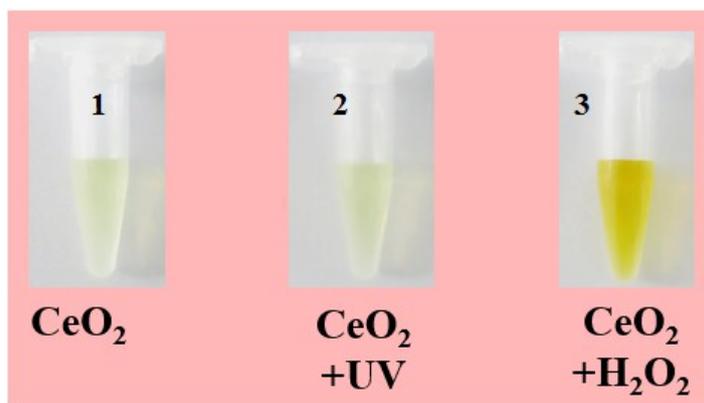


Figure S7. Photographs of nanoceria solutions under different condition; (Since the color of CeO₂ NPs solution is highly dependent on the oxidation state between Ce³⁺ and Ce⁴⁺. We can quickly judge the change of oxidation state based on the color of CeO₂ NPs solution. Based on our results, we could infer that there was no significant impact on the oxidation state of nanoceria upon the photoexcitation. However, in the presence of H₂O₂, rapid color change (from colorless to yellow) was observed, which is mainly due to a change in the oxidation state from Ce³⁺ to Ce⁴⁺.)

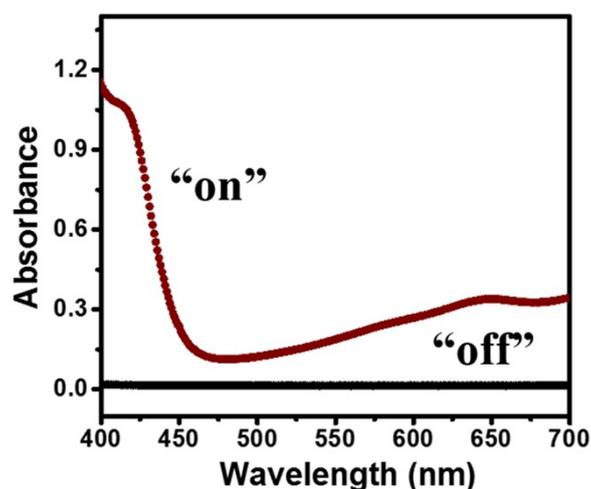


Figure S8. The catalytic ability of 2-NBA/CeO₂ hybrid system before and after the excitation of ultraviolet light toward the oxidation of ABTS. [Initial pH] = 7.0, [Phosphate buffer] = 0.5 mM.

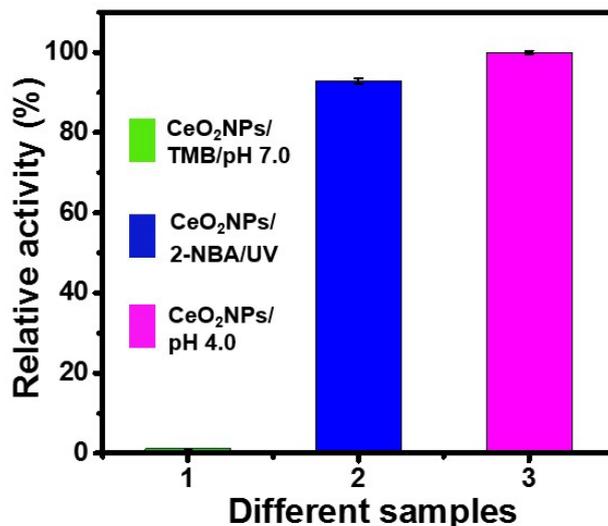


Figure S9. The relative catalytic activities of TMB reaction solutions under different conditions. The initial pH is 7.0 unless otherwise stated. [Nanoceria] = 0.1 mg/mL, [TMB] = 1 mM, [2-NBA] = 4 mM, [Citrate buffer] = 0.5 mM.

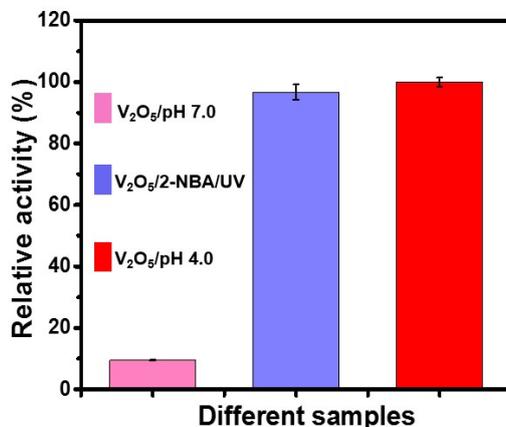


Figure S10. The relative catalytic activities of TMB reaction solutions under different conditions. The initial pH is 7.0 unless otherwise stated. [V₂O₅ nanowires] = 0.1 mg/mL, [TMB] = 1 mM, [2-NBA] = 4 mM, [Phosphate buffer] = 0.5 mM. (Our results indicated that the peroxidase-like activity of V₂O₅ nanowires could also be switched by UV light in the presence of flash photolysis reagents and H₂O₂.)

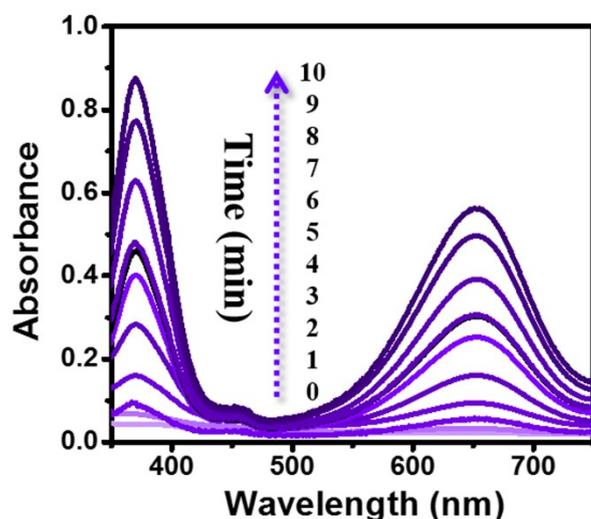


Figure S11. The catalytic ability of 2-NBA/CeO₂ hybrid system under different illuminating time toward the oxidation of substrate TMB. [Initial pH] = 7.0, [Nanoceria] = 0.1 mg/mL, [TMB] = 1 mM, [2-NBA] = 4 mM, [Phosphate buffer] = 0.5 mM.

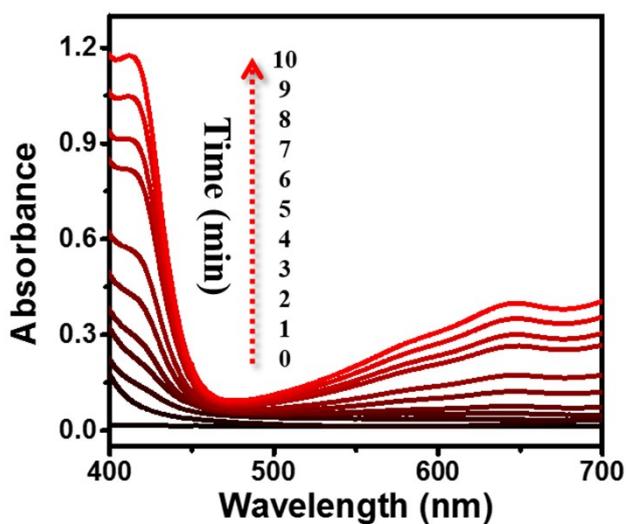


Figure S12. The catalytic ability of 2-NBA/CeO₂ hybrid system under different illuminating time toward the oxidation of substrate ABTS. [Initial pH] = 7.0, [Nanoceria] = 0.1 mg/mL, [ABTS] = 1 mM, [2-NBA] = 4 mM, [Phosphate buffer] = 0.5 mM.

1. J. M. Perez, A. Asati, S. Nath and C. Kaittanis, *Small*, 2008, **4**, 552-556.