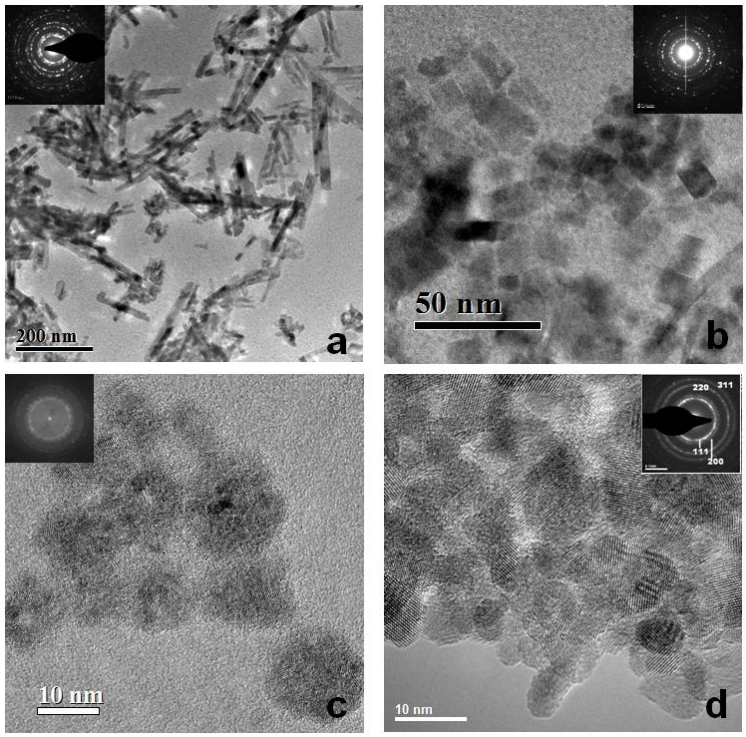
Electronic Supplemental Information

Preparation of cerium oxide nanoparticles (CNPs). Preparations of CNPs produced from two synthetic procedures were tested that have been previously described [11]. CNPs in preparation A had a higher +3/+4 redox-state ratio compared to preparation B. CNP preparations A and B were prepared by Dr. Sudipta Seal (Nanoscience Technology Center, UCF) and are identical to those used in the previous study[11]. All samples were sonicated for 45 minutes to 1 hour prior to each experiment (Branson 8510 sonifier) to prevent agglomeration, which could affect the surface area to volume ratio and thus catalytic activity of the nanoparticles.

Preparation of ceria nanorods and nanocubes: Cerium oxide nanorods and nanocubes were prepared using hydrothermal procedure (Z. Yang et al Nanotechnology, 2007, 18, 185606). The cerium to sodium hydroxide ratio was varied to change the morphology from rods to cubes. In a typical process cerium nitrate hexahydrate (Sigma Aldrich 99.9%) was dissolved in water and transferred to the Teflon beaker (Parr Instruments stainless steel autoclave reactor). Concentrated sodium hydroxide solution was then added to solution to obtain a final molar ratio of 1:10 (Ce: NaOH) (for nanorods) and 1:50 (for nanocubes) and the reactor was heated at 120^{o}C for 24-36 hours. The vessel was allowed to cool to room temperature and the final product was washed multiple times with DI water until the pH of the filtrate was close to neutral. The final product after washing was dried at 300^{o}C and characterized using transmission electron microscope.

Transmission Electron Microscopy: The particle morphology was analyzed with a FEI Technai F30 high resolution transmission electron microscope (HRTEM) operated at

300KV with a point to point resolution of 0.2nm. The samples for TEM were prepared by drop coating the suspension of cerium oxide nanoparticles on a holey carbon coated copper grids. The grids were dried in vacuum for 24 hrs before HRTEM imaging. TEM images (Figure SI-2) shows the nanorods, nanocubes, nanoparticle A and B morphology.



SI Figure 1. High Resolution Transmission Electron Micrographs of cerium oxide nanoparticles of various morphologies a) nanorods b) nanocubes c) sample A d) sample B. Morphology of several preparations of cerium oxide nanoparticles are shown using HRTEM. Rods (aspect ratio 1: 5) and cubes (30-50 nm) are observed (A and B) while sample A has 3-5 nm nanoceria particles agglomerated in 10-15 nm clusters. Sample B has spherical to irregular nanoparticles about 5-7 nm in size. Inset confirms the fluorite lattice structure of cerium oxide.

UV-Visible spectrophotometry. A Hewlett-Packard diode array UV-visible 8453 spectrophotometer was used to follow the concentration of H_2O_2 (Acros Organics) at its absorbance maximum of 240 nm. 100 μL samples containing hydrogen peroxide (Acros Organics) and nanoceria were mixed with 50 mM tris(hydroxymethyl)aminomethane (Tris, pH 7.0) to buffer the reaction and the chelating agent 1 mM diethylene triamine pentaacetic acid (DTPA) to prevent potential interference by adventitious metals or cerium that could leach from the particles during catalysis. Prepared mixtures were loaded in 40 μL quartz cells (Starna Cells, Inc) and each sample was analyzed for approximately 600 seconds, with absorbance readings taken at constant time intervals in order to generate kinetic data of the levels of H_2O_2.

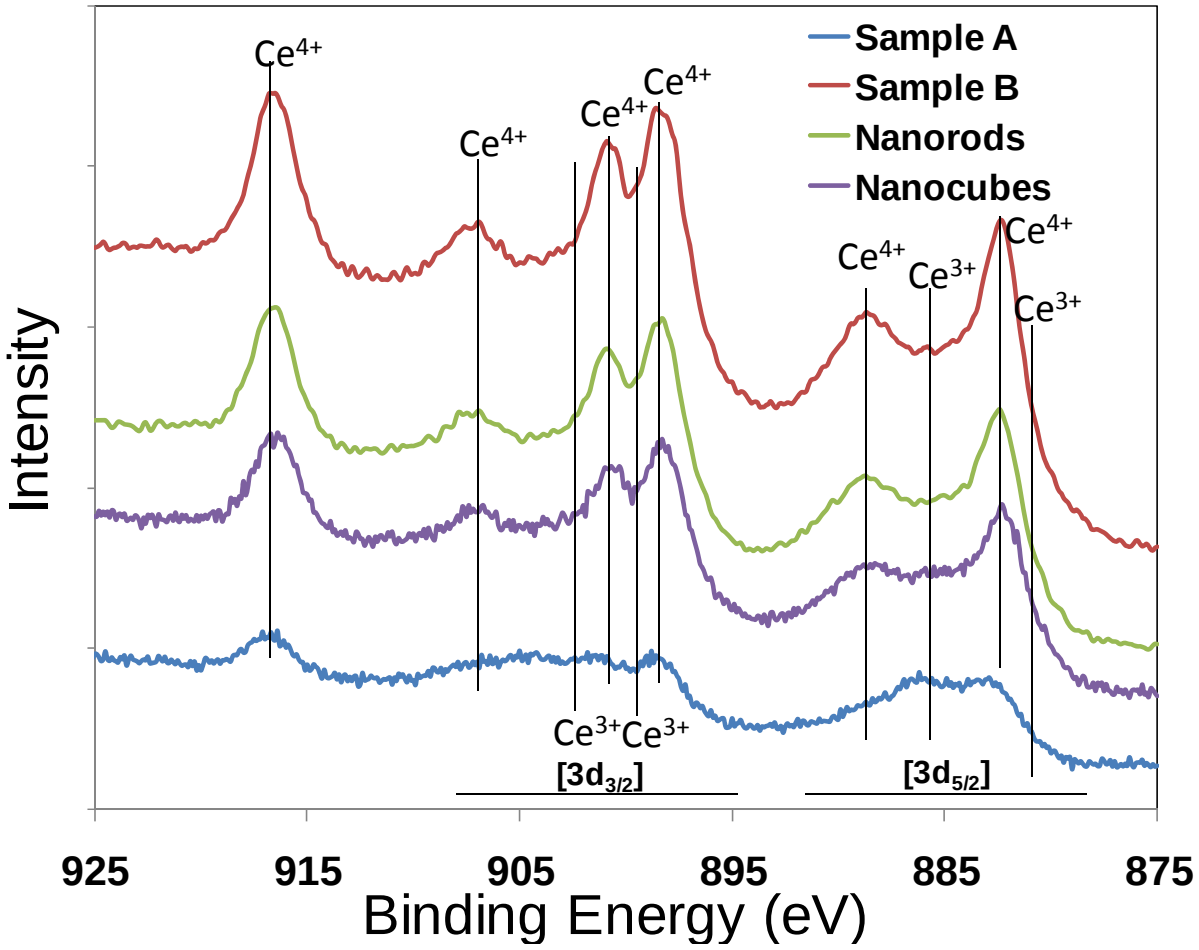
Amplex Red assay. The Amplex Red Hydrogen Peroxide/Peroxidase assay kit (Invitrogen, Eugene, Oregon) was also used to measure H_2O_2 levels. The Amplex Red reagent (10-acetyl-3,7-dihydroxyphenoxazine) reacts with H_2O_2, in the presence of horseradish peroxidase (HRP), to produce the fluorophore resorufin. Dimethyl sulfoxide (DMSO) and 0.25 M sodium phosphate were used as a solvent and buffer, respectively. A Varian Cary Eclipse fluorescence spectrophotometer was used to detect the fluorescence of resorufin (excitation at 571 nm and emission at 585 nm), which was indicative of the H_2O_2 levels in the samples. A H_2O_2 standard curve was generated and used to determine the H_2O_2 concentration in each sample. Samples were assayed in 96-well plates, and kinetic data was obtained by adding H_2O_2 to nanoceria samples pre-incubated in buffer. Samples were taken at 10-minute intervals and assayed for changes in peroxide levels. The Amplex Red reagent and HRP were then added and allowed to incubate for 30 minutes before the fluorescence readings were taken. Due to the

unreliability of this assay at high levels of H_2O_2, the final concentration of H_2O_2 in each sample that was used was 2 μM. 50 mM Tris and 1 mM DTPA were included in the reaction buffer as indicated above.

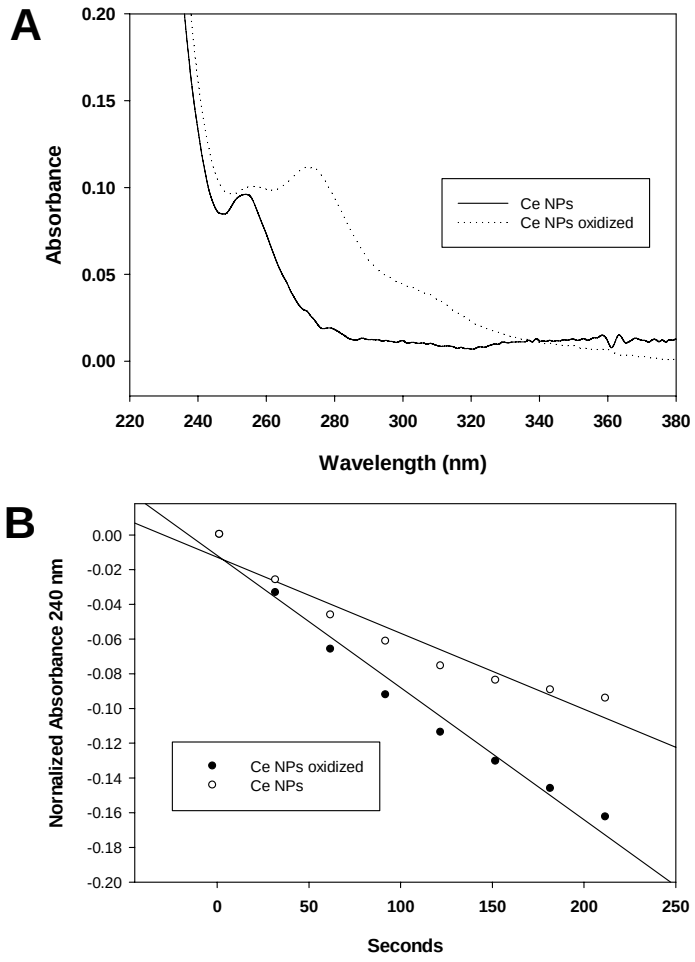
Dissolved oxygen measurement. To follow the release of oxygen, we utilized a dissolved oxygen probe. A DO-166MT-1 micro dissolved oxygen probe (Lazar) was used to measure the oxygen levels in a buffered reaction as described above. The probe was inserted into a small beaker with a 10 mL sample containing hydrogen peroxide in buffer, and the dissolved oxygen levels were allowed to stabilize for at least one hour before the addition of nanoceria. The results were then subjected to a Weibull peak dynamic fit curve using SigmaPlot 10 (Systat Software, Inc.).

Estimation of Ce3+ and Ce4+ concentration using X-ray Photoelectron Spectroscopy (XPS) – The oxidation state of cerium in CNPs were gauged from XPS analysis of the samples using PHI ESCA 5400 spectrophotometer operated at 300W at a base pressure of 2 x 10^{-8} torr or less and Al Kα as source of x-rays. The samples for the XPS analysis were prepared in glove box with continuous flow of argon by drop coating a 5mM suspension of CNPs on a silicon wafer. The samples were dried while coating until a reasonably thick coating could be observed visually. Equal amount of sample from each of the preparation was dropped on silicon wafer. The samples were then transferred to a sealed sample transfer chamber inside the glove box for transferring to the XPS chamber without any exposure to ambient atmosphere to avoid any interference of atmosphere with the valence chemistry of cerium. The spectrophotometer was calibrated using a gold standard prior to XPS run and any charge shift in the samples was corrected using adventitious carbon as a reference at binding energy of 284.6 eV. The XPS

spectrum of cerium is shown in SI -1 and depicts the higher amount of Ce^{3+} oxidation state in sample A. The XPS spectrum from cerium is complex and split into $Ce3d_{3/2}$ and $Ce3d_{5/2}$ with multiple shake-up and shake-down satellites. The peaks between 875 and 895 eV belong to the Ce $3d_{5/2}$ while peaks between 895–910 eV correspond to the Ce $3d_{3/2}$ levels [P. Burroughs et al JCS Dalton, 1976, **17**, 1686]. The peak at 916 eV is a characteristic satellite peak indicating the presence of cerium (IV) however, for estimation of cerium content the main peaks from only the $3d_{5/2}$ portion of the spectrum were used for the peak fit. $3d_{5/2}$ portion of each spectrum was fitted and the ratio of Ce^{3+} to Ce^{4+} was calculated from the integrated area under the peak. A general practice for using the entire spectrum containing satellite peaks suffer from a huge background problem with varying FWHM and may lead to over or underestimation of Ce^{3+} content. The peaks were fitted using Peakfit 3.0 version and the relative concentration was estimated for all the samples as listed in table 2 in the main document.



SI Figure 2. Raw XPS spectra from various nano ceria samples. The peaks between 875 and 895 eV belong to the Ce $3d_{5/2}$ while peaks between 895–910 eV correspond to the Ce $3d_{3/2}$ energy levels. The higher extent of Ce3+ oxidation state in nanoceria preparation A could be easily seen with contribution from peaks at 880.1 ±0.5, 885.2± 0.3, 900.1± 0.5and 903.5± 0.3eV.



SI Figure 3. Chemical conversion of Ce NPs from +3 to +4 state in phosphate solution leads to improved catalase mimetic activity. (A) After 72 hours of incubation in phosphate buffered saline (PBS), the level of cerium atoms in the +3 oxidation state is shifted to +4 state. (B) When tested for their ability to react with hydrogen peroxide, treated Ce NPs are improved. The mean of three independent experiments is shown and the conversion of the material was repeated three times to confirm changes that occur in the oxidation state.