Supporting Information

Self-assembled Porous Ceria Nanostructures with Excellent Water-solubility and Antioxidant Properties

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1. Experimental section

1.1 Synthesis of β-CDs functionalized nanoceria

β-CDs functionalized nanoceria with porous structure was prepared using a simple one-pot hydrothermal method. In a typical synthesis, 1 mmol Cerium (III) nitrate hexahydrate (Aldrich, 99%) and 1 mmol β-CDs (Aldrich, ≥98%) was dissolved in 15 mL of deionized water under vigorous stirring at room temperature. 0.6 g NaOH was added gradually into the above mixed solutions under vigorous stirring. Sequentially, the colloidal precipitates, which still exist in the solution, were further vigorously stirred for 5 min. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 120 °C for 6 h and then cooled to room temperature naturally. To decrease the toxicity to the tested cell, the fresh gray precipitates were separated by centrifugation and washed with deionized water and 2 % salt solution alternatively to remove ionic remnants.

1.2 Characterization

X-ray powder diffraction (XRD) was carried out on an XRD-6000 X-ray diffractometer with Cu Kα radiation (λ=1.54060Å) at a scanning rate of 0.05^{o} s^{-1}. Scanning electron microscopy (SEM, HITACHI S-4800) and transmission electron microscopy (TEM, FEI TECNAI G20) were performed. Infrared spectra were taken on a Fourier transform infrared spectrophotometer (SHIMSDZU 8400 S).

XPS was performed in a Physical Electronics 5400 ESCA spectrometer with a base pressure of 109 Torr and MgKα X-ray radiation at a power of 200 W. Specific surface areas and pore size distribution were computed from the results of N_2 physisorption at 77 K (model: BECKMAN SA3100 COULTER) using the BET (Brunauer–Emmet–Teller) and BJH (Barrett–Joyner–Halenda) formalisms, respectively.

1.3 Autocatalytic activity test

The autocatalytic activity was assessed by treating a 10 mg/ml solution of β-CDs functionalized nanoceria with 0.1 M of H_2O_2 solution. The percentage transmittance was then monitored upon addition of hydrogen peroxide at 0 h, 10 days, and 20 days. The UV-vis spectra of the obtained samples dispersed in deionized water were recorded on a SHIMADZU UV-2501 spectrometer using a quartz cell (1 cm path length). Deionized water was used as a reference.

1.4 Cellar viability and ROS levels measure

Cellular viability was determined by the MTT assay. Briefly, 1×10^4 cells were plated onto 96 multiwell plates. After incubation with the indicated doses of nanoceria for 24 or 48 h at 37 °C, the original culture medium is removed and washed the cells twice by fresh culture medium. Then, fresh culture medium and MTT were added into each well containing cell and incubate for another 3 h. Remove media with needle and syringe. Next, add dimethyl sulphoxide (DMSO) to each well and pipette up and down to dissolve crytals. Put plate into the incubator for 5min to dissovle air bubbles. Finally, transfer to plate reader and measure absorbance at wavelength between 500 and 600 nm.

ROS levels were measured using DCF fluorescence (Sigma). 1×10^4 RAW cells were plated onto 12 multiwell plates for 4h. After incubation with the indicated doses of nanoceria for 6 h at 37 °C, removing the original culture medium, washing the cells twice by fresh culture medium, and

adding fresh DMEM culture medium, the cells were incubated for 20 min. ROS were measured by dihydro 20, 70-dichlorofluorescin diacetate (H_2DCFDA, excitation 492 nm/emission 517 nm), which is a cell-permeable dye, when it is de-exterified and oxidized to dichlorofluorescein (DCF) by intracellular ROS, it can fluoresce. All of the probes were incubated at 37 °C in dark for 40 min. Cells were centrifugated with 1000 rpm for 3 min and washed twice by PBS to remove the probes that were not enter into the cells. Finally, the cells were analyzed by flow cytometer. Mean absorbance of non-exposed cells served as the reference value for calculating 100 % cellular viability.

2. Additional Figures and Figure Captions

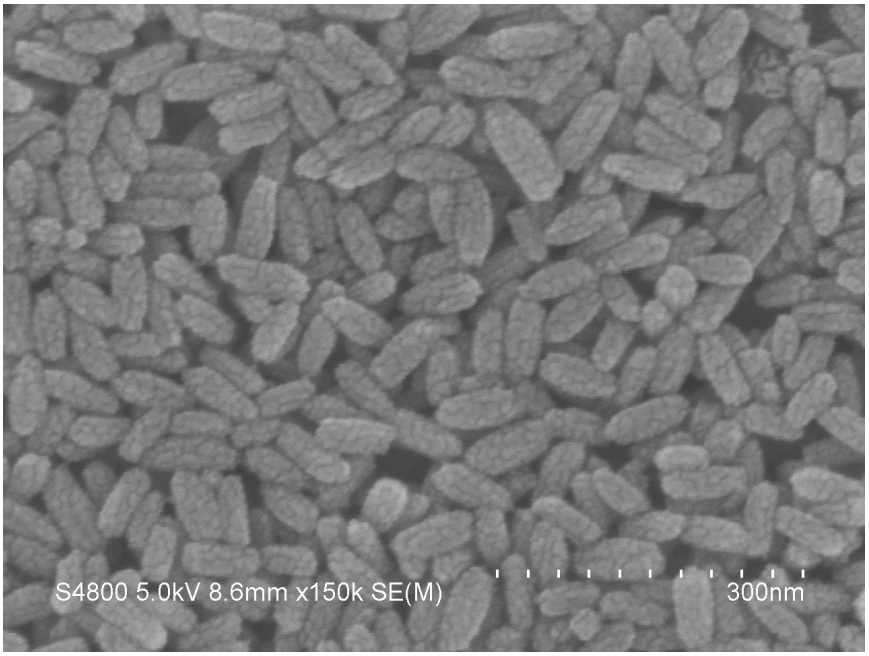

Fig. S1. High-magnification SEM images of the obtained nanoceria.

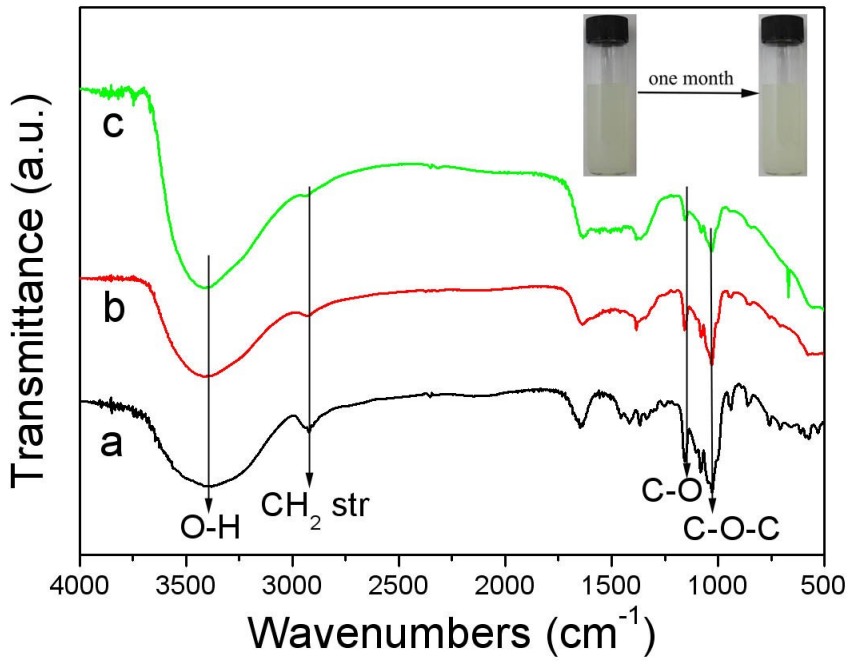

Fig. S2. FT-IR spectra of β-CDs (a); as-prepared β-CDs coated nanoceria (b); and β-CDs coated nanoceria after using as antioxidant (c).

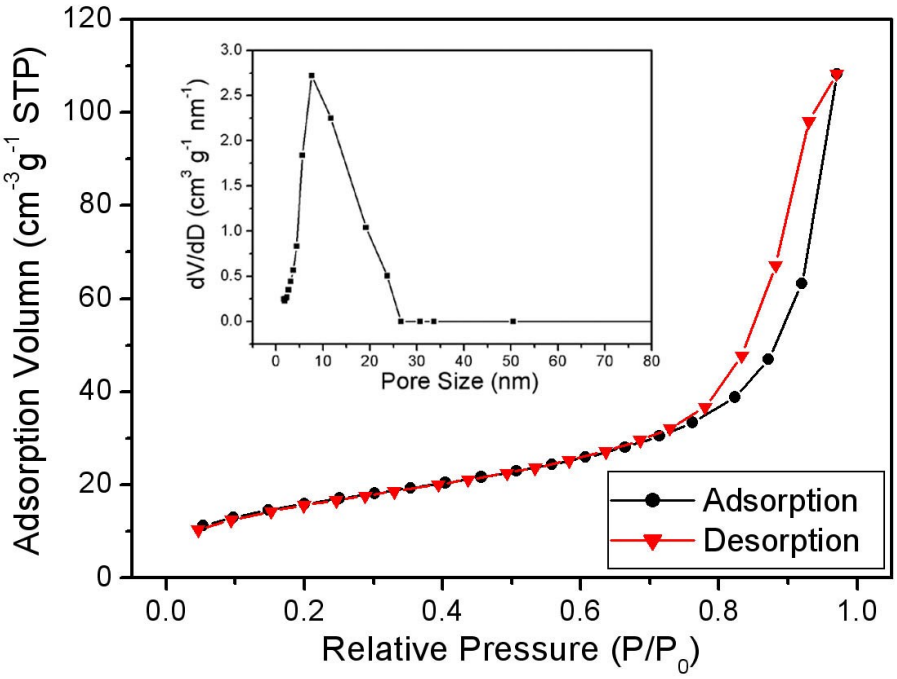

Fig. S3. N_2 adsorption-desorption isothermal curves of porous β-CDs coating nanoceria corncob. The inset shows the corresponding pore size distribution.

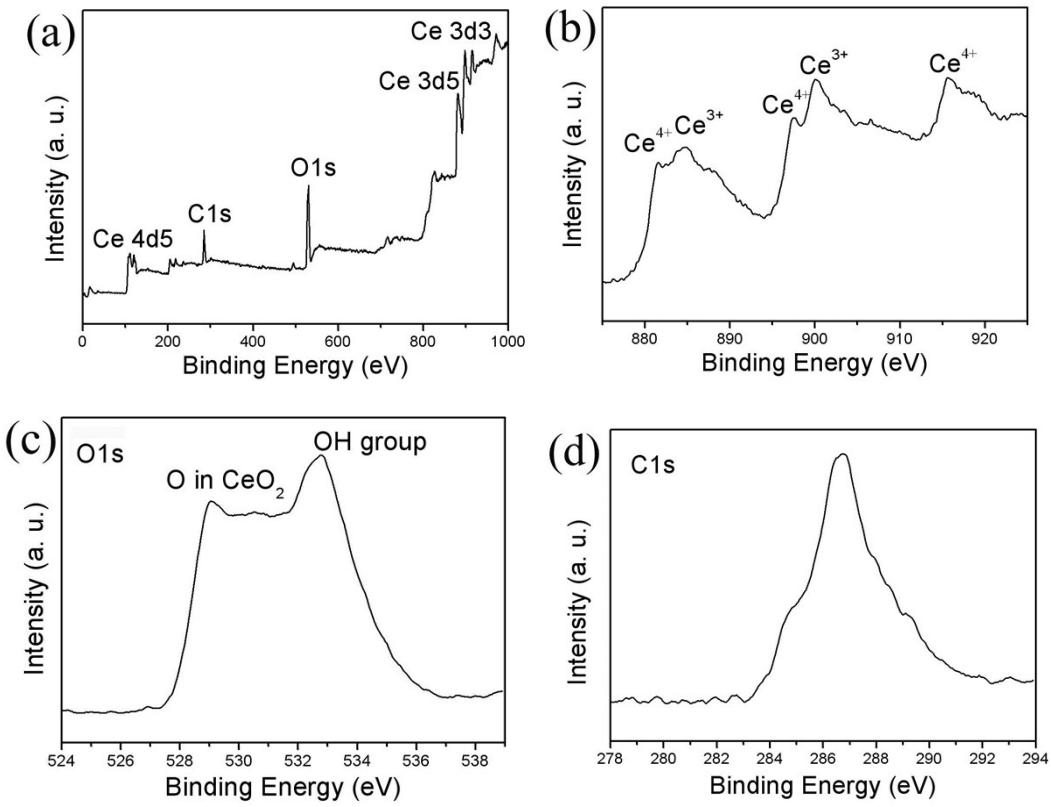

Fig. S4. XPS spectra of the nanoceria: (a) the survey scan spectrum of the synthesized samples, (b-d) high-resolution XPS spectrum shown different valence states for Ce, O, and C.

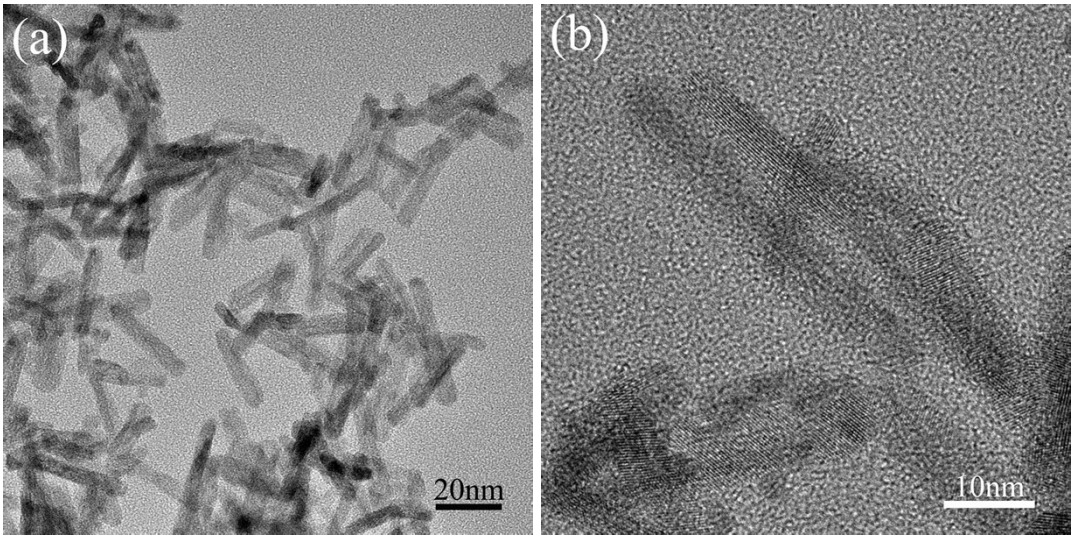

Fig. S5. TEM images of CeO_2 nanorods without β-CDs prepared by hydrothermal method at 120°C for 6 h.

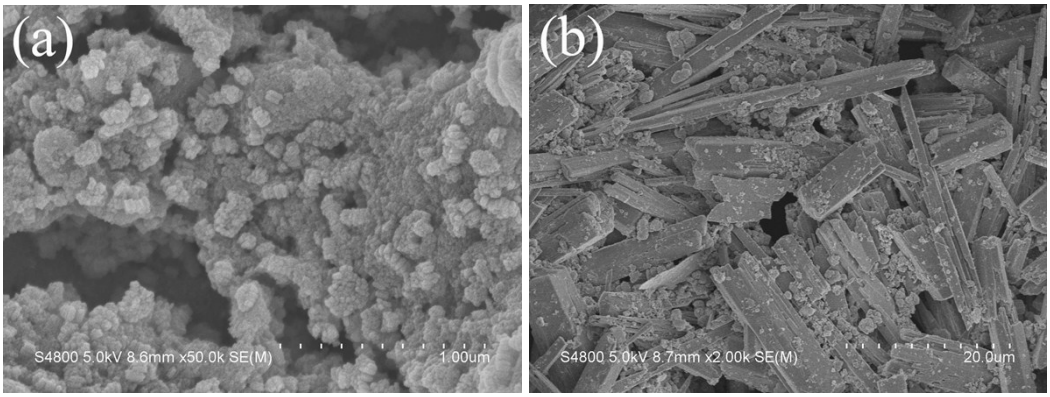

Fig. S6. SEM images of the products prepared by hydrothermal method at 1mmol β-CDs and 0.6g NaOH for 6 h. (a) 80°C, (b) 220°C.

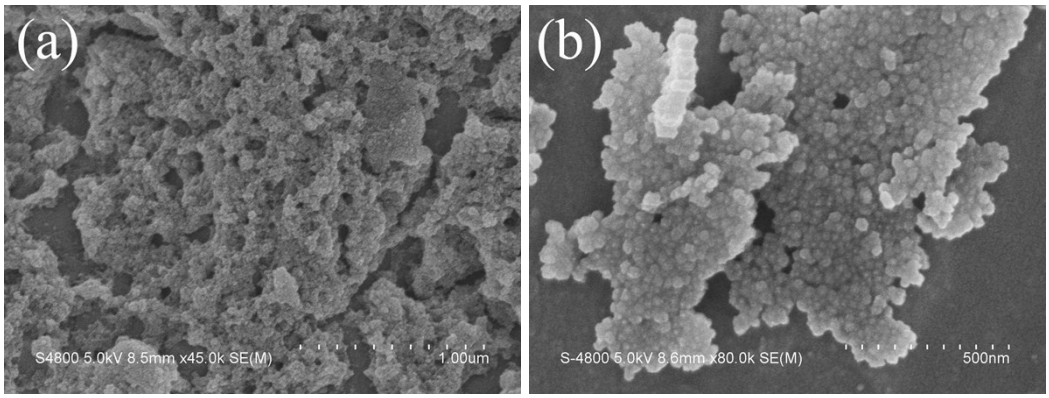

Fig. S7. SEM images of the products prepared by hydrothermal method at 120°C in the presence of 1mmol β-CDs for 6 h. (a) 0.1g NaOH, (b) 2.4g NaOH.

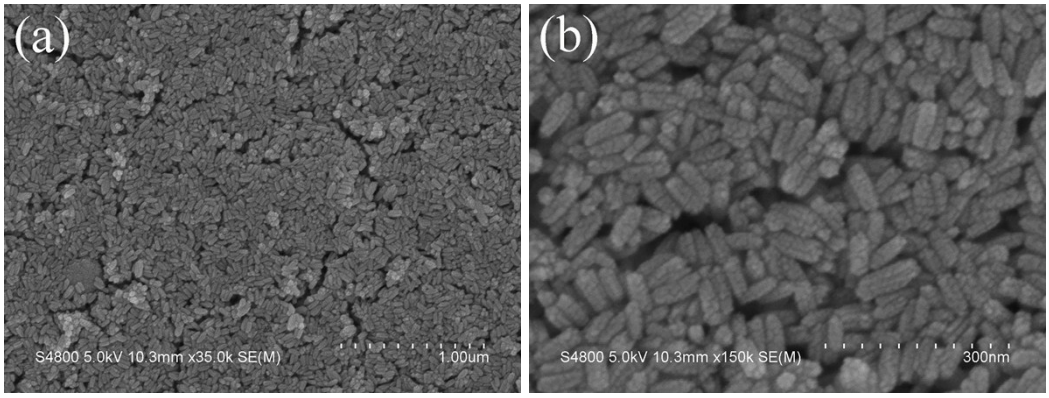

Fig. S8 SEM images of the products prepared by hydrothermal method at 100°C with the presence of 0.3g NaOH, and 2mmol β-CDs for 24 h.

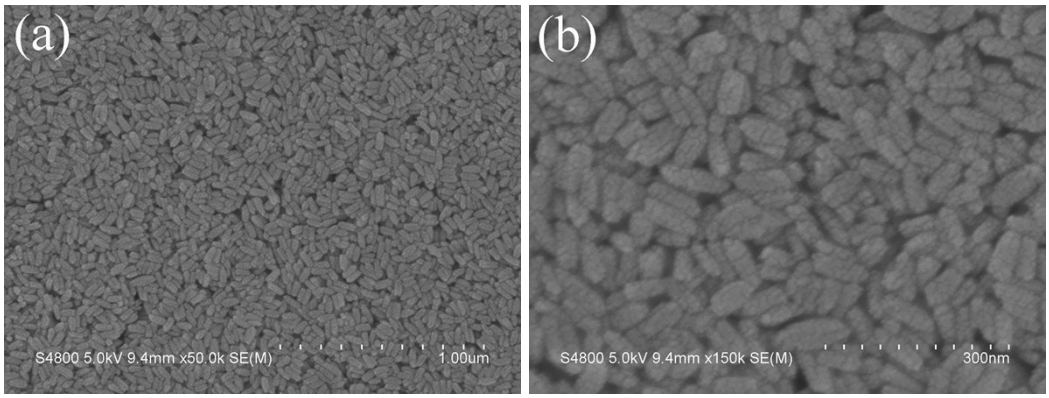

Fig. S9. SEM images of the products prepared by hydrothermal method at 140°Cwith the presence of 0.6g NaOH and 1mmol β-CDs for 12 h.

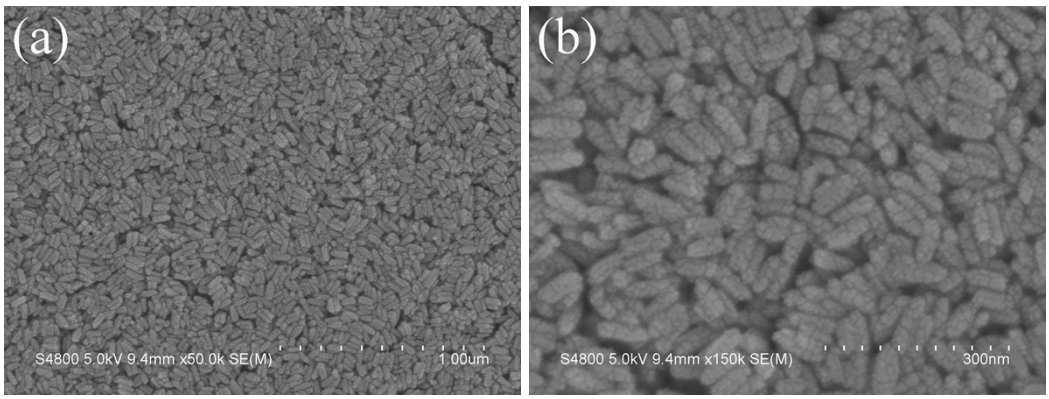

Fig. S10. SEM images of the products prepared by hydrothermal method at 180°C with the presence of1.2g NaOH and 0.5mmol β-CDs for 6 h.

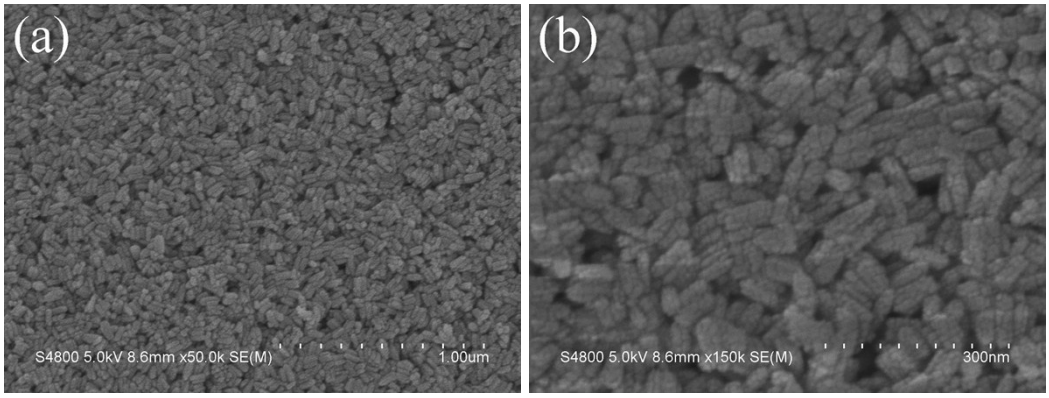

Fig. S11. SEM images of the products prepared by hydrothermal method at 200°C with the presence of 0.6g NaOH and 1mmol β-CDs for 6 h.

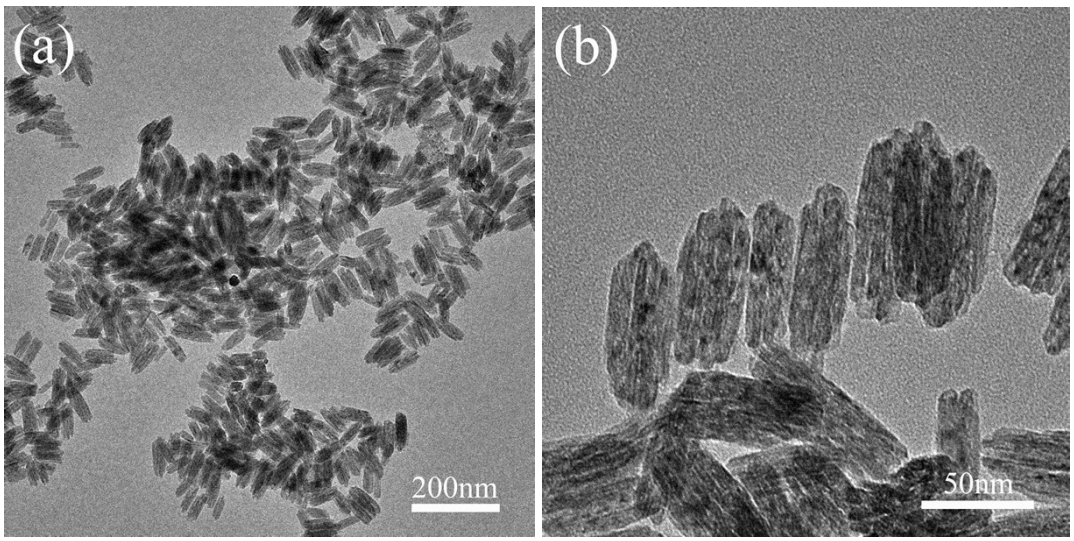

Fig. S12. TEM images of the samples after catalysis.

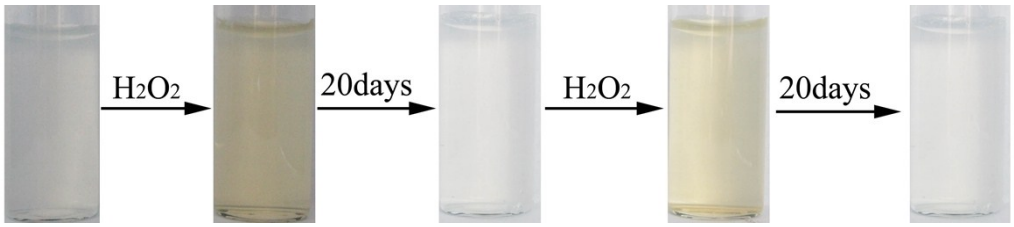

Fig. S13. Reversible color changes in a solution of β-CDs coated nanoceria upon addition of hydrogen peroxide.

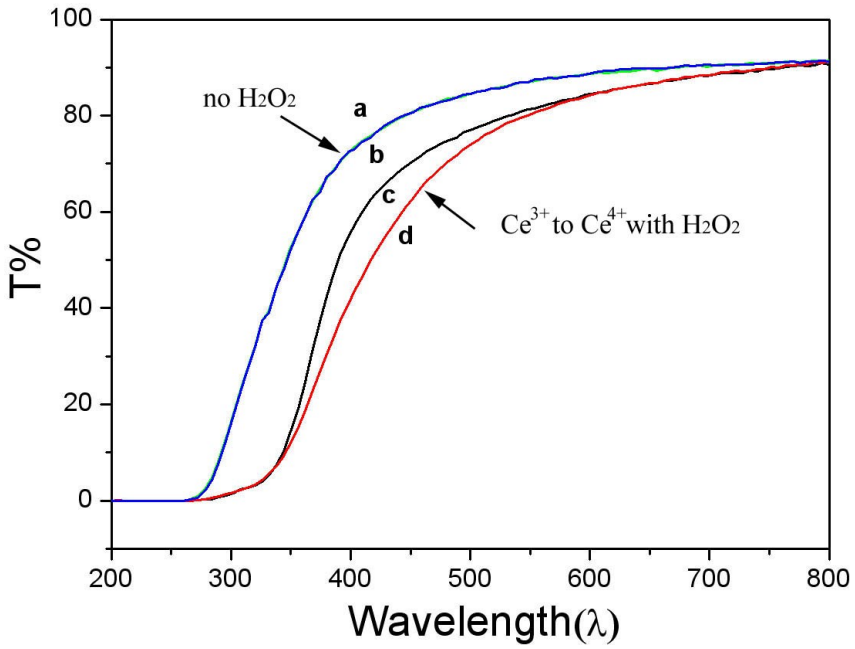

Fig. S14. The UV−visible transmittance spectrum of (a) as-prepared samples aqueous suspensions (green line); (b) the samples injected H_2O_2 after 20 days (blue line); (c) the samples injected H_2O_2 after 10 days (black line); (d) the samples injected H_2O_2 (red line).

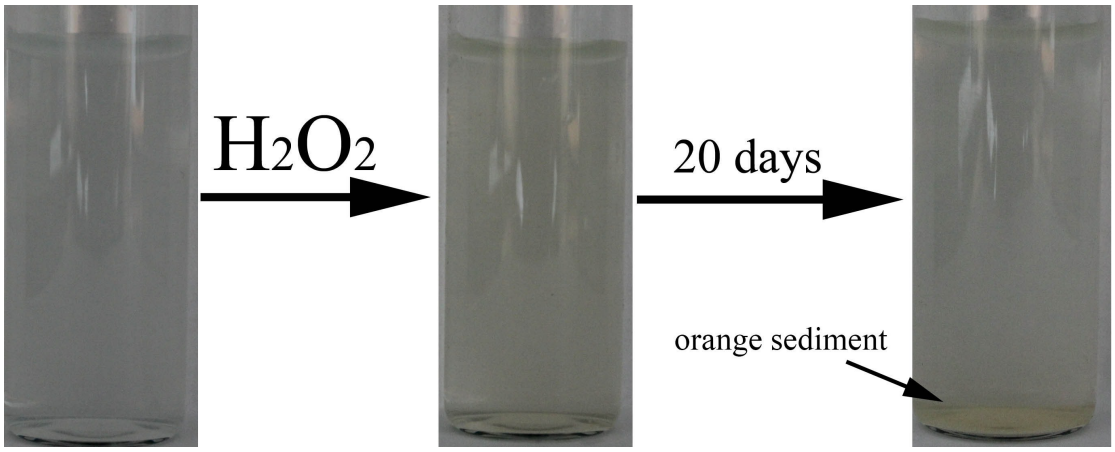

Fig. S15. The color changes in a solution of the ceria nanorods without capping β-CDs upon addition of hydrogen peroxide.