X-ray absorption study of ceria nanorods on promoting the disproportionation of hydrogen peroxide

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Electronic Supplementary Information

Experimental Methods

1. Materials

Cerium (III) sulfate hydrate ($Ce_2(SO_4)_3 \cdot$ x H_2O) and sodium hydroxide (NaOH) were purchased from Sigma–Aldrich (St. Louis, MO). Hydrogen peroxide aqueous solutions (H_2O_2, 30% w/w) were purchased from VWR SP and Showa Chemical Co. (Tokyo, Japan). Trizma base (≥99.9%) was obtained from Sigma-Aldrich (Tokyo, Japan). All chemicals were used without further purification. Ultrapure water with a resistivity greater than 18 MΩ·cm at 25 °C was used in the experiment. It was purified from house deionized water using a Synergy Millipore system (EMD Millipore, Billerica MA).

2. Ceria nanorods synthetic method

The nanostructured ceria support was synthesized using a previously reported hydrothermal method.[1] 0.5 g of $Ce_2(SO_4)_3 \cdot x\ H_2O$ were mixed with 40 mL of 10 M NaOH solution in a 50-mL Teflon-lined stainless steel autoclave. The chemicals in the autoclave were then hydrothermally treated at 120 °C for 15 h in a convection oven. The product was filtered and rinsed with 50 mL of water. Afterwards, it was placed in the convection oven for an initial oxidation at 50 °C for 2 h. 25 mL of ultrapure water and 25 mL of 30 % H_2O_2 were then added to the oxidized product and sonicated for 30 min, followed by stirring for 1 h to enable the reaction to reach completion. The resulting sample was filtered with a 3.0-μm pore size polycarbonate membrane, rinsed with water and dried at 50 °C for 4 h in the convection oven. At the end, the synthesized material was activated at 400 °C in simulated air (20% O_2, 80% N_2) for 30 min at a pressure of 0.07 Torr.

3. Characterization methods

TEM was used to investigate the morphology of the synthesized particles. About 5 mg of sample was dispersed in ethanol, and sonicated for 10 s for better dispersion. 10 μL of the suspension was pipetted and loaded on holey carbon films supported on Cu TEM grids. The TEM images were recorded on a Hitachi H-7500 transmission electron microscope (Hitachi High Technologies America, Pleasanton, CA) operating at 80 kV. The HRTEM images were recorded on a Tecnai G2 F20 S-Twin 200 kV field-emission transmission electron microscope (FEI Company, Hillsboro, OR). The images were analyzed with the DigitalMicrograph software (Gatan, Inc., Pleasanton, CA). The crystalline structures of the samples were investigated by X-ray powder diffraction (XRD) using a Rigaku D/Max-B X-ray diffractometer (Rigaku Americas, The Woodlands, TX) equipped with a Cu Kα X-ray source (average wavelength = 1.544 Å).

The chemical states of Ce and local structures surrounding Ce in ceria samples were probed by using the X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) techniques. The Ce L_3-edge XANES and EXAFS measurements were performed at beamline BL17C of the Taiwan light source at National Synchrotron Radiation Research Center in Taiwan. A Si (111) Double Crystal Monochromator (DCM) was used to scan the photon energy. The energy resolution ($\Delta E/E$) for the incident X-ray photons was estimated to

be 2×10^{-4}. The EXAFS spectra were measured in the fluorescence mode using a Lytle fluorescence detector for ceria samples. The *IFEFFIT* software package was used to analyze the EXAFS data to obtain the local structural parameters of ceria. Several constraints were applied to the fitting parameters to exclude unphysical results. The Debye-Waller factors of the first and the second shell were set to be the same, while the energy shifts (ΔE) that largely depended on the atomic species for the first and second O shells were set identically.

4. Analysis of the concentrations of cerium ions in the reaction mixtures

Inductively coupled plasma- mass spectrometry (ICP-MS) (Bruker Aurora M90) was applied to analyze the concentration of Ce ions in the reaction mixtures of ceria nanorods and 10 mM H_2O_2/ 0.1 M Tris buffer (pH = 7.54). Two samples were prepared identically to obtain solution mixtures of 1 g/L ceria nanorods in 10 mM H_2O_2/ 0.1M Tris buffer (20 mL 0.1 M Tris buffer (pH = 7.54), 20 mg of ceria nanorods, and 22.8 μL 30% H_2O_2). Under ambient conditions, one sample was allowed to stir for 1 h, while the other one was allowed to stir for 10 h. Two control samples of 1 g/L ceria in 0.1 M Tris buffer (pH = 7.54) with 1-h and 10-h long stirring periods were also prepared. All four solutions were centrifuged for 20 min at 2500 rpm and the supernatants were then filtered through 0.2 μm PTFE filters to remove ceria nanorods. ICP-MS analysis was used to determine the concentration of Ce ions in these samples. First, a three point calibration curve was obtained using standard aqueous solutions with concentrations of 10, 100, and 1000 ppb of Ce. Second, three control solutions (18 M$\Omega \bullet$ cm H_2O, 0.1 M Tris buffer (pH = 7.54), and 10 mM H_2O_2/ 0.1 M Tris buffer (pH = 7.54)) were analyzed and were shown to have less than 1 ppb of Ce. Lastly, the four solution samples obtained from the ceria nanorod solution mixtures were analyzed and their concentrations of Ce ions were also determined to be less than 1 ppb.
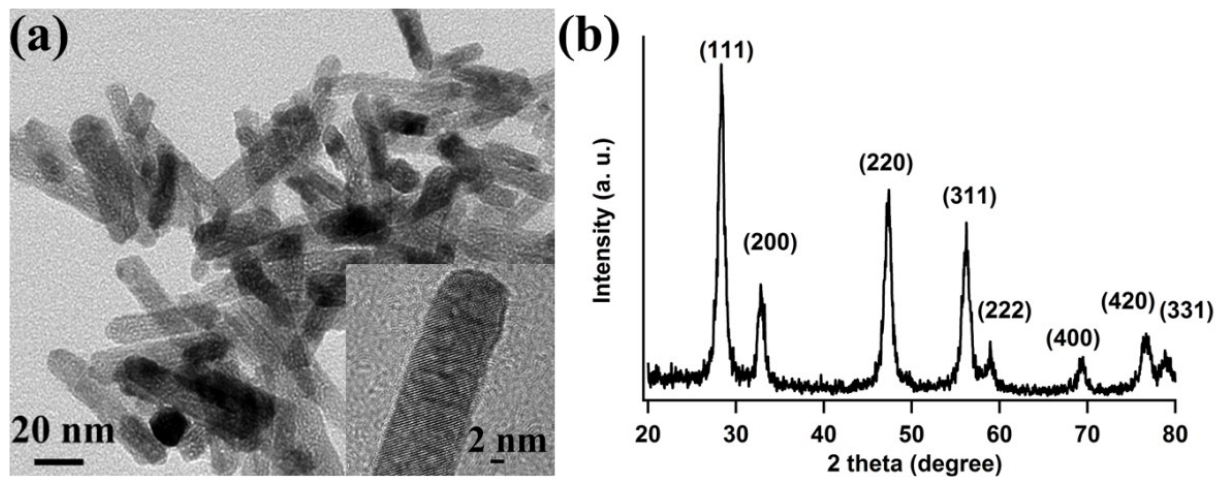
Fig. S1 (a) TEM image of ceria nanorods. (inset) HRTEM image of a ceria nanorod. (b) XRD pattern of ceria nanorods. All XRD peaks were indexed with respect to the cubic $Fm\bar{3}m$ structure of CeO_2. ICDD card 04-013-4361 was used for the peak assignments for the CeO_2 content in the patterns.
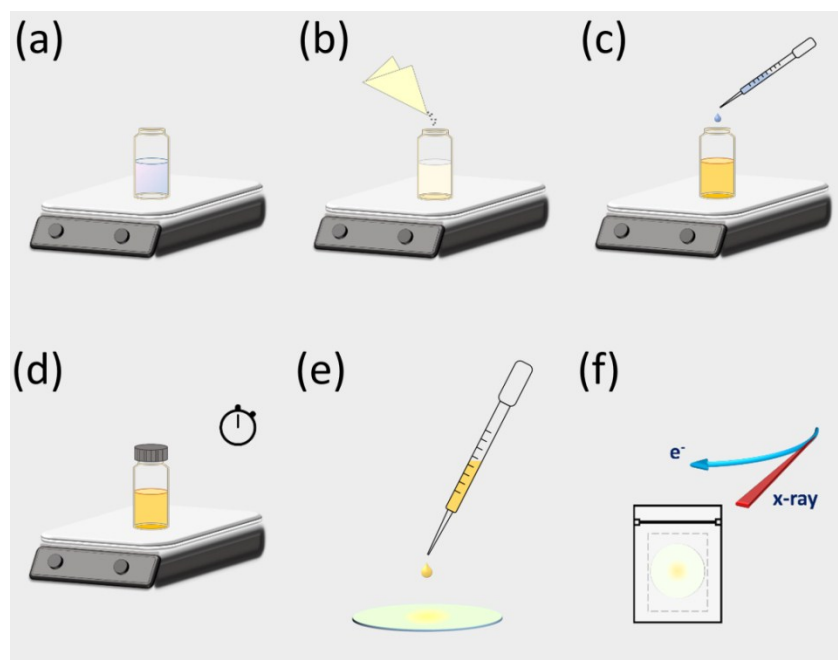
Fig. S2 Scheme of the ceria sample preparation procedure for the XANES and EXAFS experiment. (a) A 20 mL 0.1 M Tris (pH= 7.54) buffer solution was prepared. (b) 20 mg of ceria nanorod sample was added to the Tris buffer solution. (c) 22.8 uL of 30 wt.% H_2O_2 (aq) was added to the solution in (b). This resulted in a 10 mM H_2O_2/ 0.1 M Tris buffer solution. Ceria nanorods reacted with the buffered H_2O_2 solution and exhibited a yellowish/orange color. (d) Record the reaction time between ceria nanorods and the buffered H_2O_2 solution. (e) After a certain reaction time (10 min, 0.5 h, 1 h, 2 h, 3 h, 5 h, 7 h and 10 h), a sample of the suspension containing ceria nanorods were pipetted out and dropped on a filter paper. (f) The sample on filter paper was transferred to a zip lock bag for an X-ray adsorption measurement while the sample remained wet.
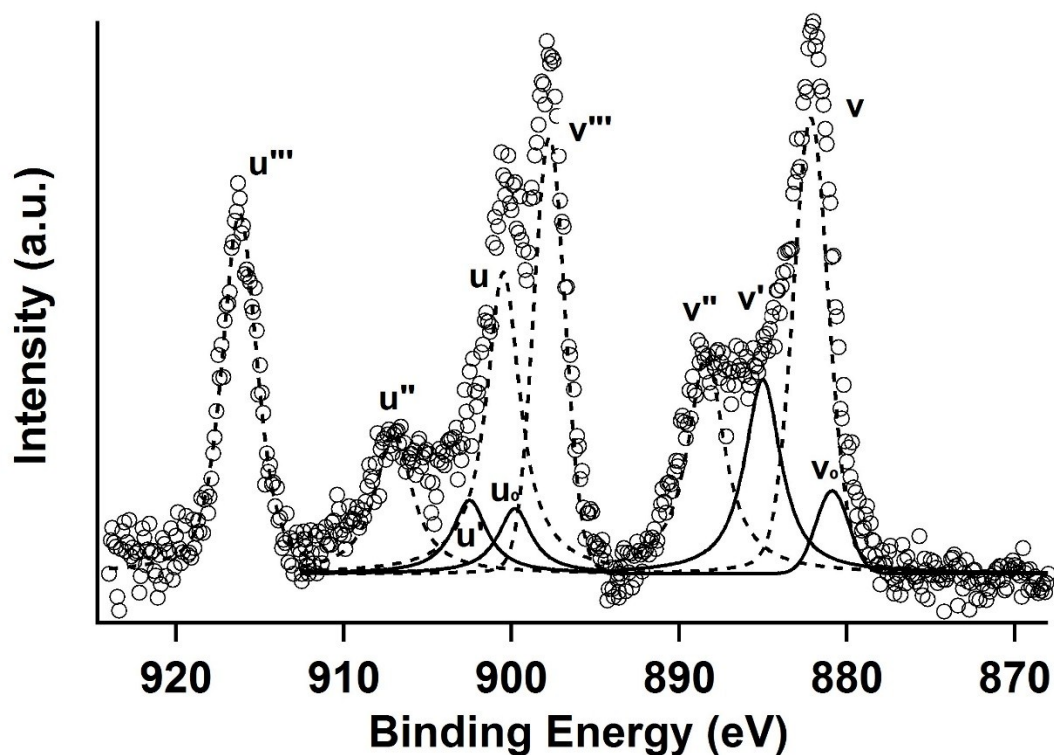
Fig. S3 Fitted Ce $3d$ core level XPS spectrum of ceria nanorods. Ce ($3d$) core levels of CeO_2 and Ce_2O_3 are fitted into main and satellite peaks. The binding energy of Ce ($3d_{5/2}$, $3d_{3/2}$) levels for CeO_2 are marked by v, v", v"' and u, u", u"' (represented by dotted lines). Peaks v_0, v' and u_0, u' (represented by solid lines) refer to Ce $3d_{5/2}$ and $3d_{3/2}$ respectively and are characteristics for Ce_2O_3.[2-4]
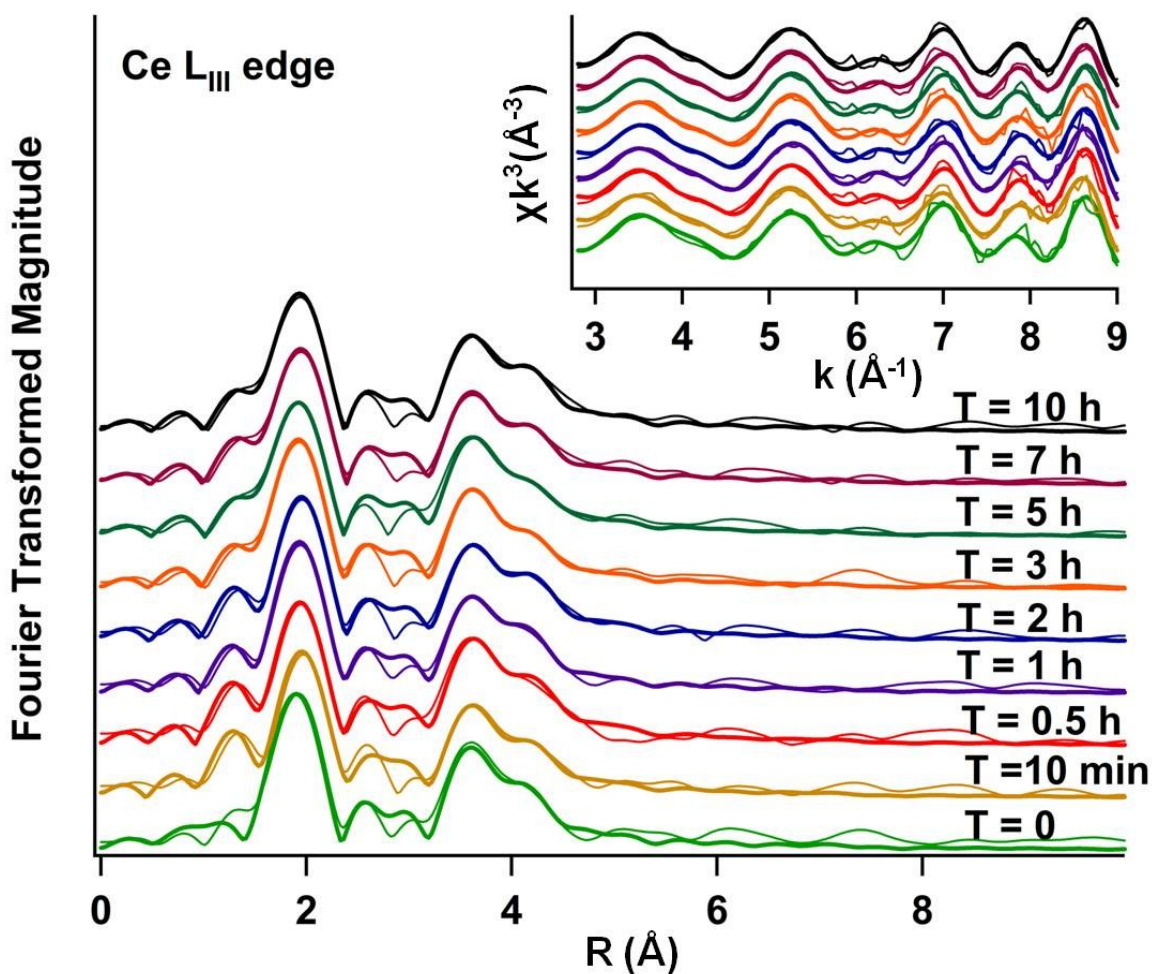
Fig. S4 Fourier transformed Ce L$_{III}$ edge EXAFS data of ceria nanorod samples from different reaction time (0 to 10 h) in a 10 mM H$_2$O$_2$/ 0.1 M Tris buffer aqueous solution. The inset image shows the EXAFS spectra of the samples in *k* space. Thick lines represent data and thin lines represent fittings.

Table S1 Structural parameters of ceria nanorods samples reacted with a 10 mM H_2O_2/ 0.1 M Tris (pH = 7.54) buffer solution from different reaction time obtained from the Ce L_{III} edge EXAFS analysis. The underline marks indicate fixed parameters when processing the fitting analysis. The larger energy shift fitting number is due to the high disorder and small particle size of ceria catalysts.

Ceria nanorods Reaction time	Atom	N	R (Å)	σ^2 (10^{-3} Å^2)	ΔE_0 (eV)
Control[a]	O	5.8 ± 0.6	2.30 ± 0.01	4.7 ± 1.2	6.0 ± 0.6
0 h	Ce	5.6 ± 0.4	3.83	1.8 ± 0.6	5.8 ± 0.4
	O	5.4 ± 1.1	4.55	1.8 ± 0.6	13.3 ± 0.7
10 min	O	0.9 ± 0.2	1.67 ± 0.02	1.7 ± 0.9	9.3 ± 0.8
	O	4.2 ± 0.3	2.34 ± 0.01	1.7 ± 0.9	9.3 ± 0.8
	Ce	4.7 ± 0.4	3.83	1.4 ± 0.5	5.4 ± 0.6
	O	4.8 ± 1.2	4.55	1.4 ± 0.5	14.6 ± 1.1
0.5 h	O	0.9 ± 0.3	1.65 ± 0.02	3.9 ± 0.8	8.2 ± 0.8
	O	4.7 ± 0.4	2.32 ± 0.01	3.9 ± 0.8	8.2 ± 0.8
	Ce	4.7 ± 0.4	3.83	1.3 ± 0.3	6.4 ± 0.6
	O	5.2 ± 1.3	4.55	1.3 ± 0.3	15.4 ± 1.0
	O	0.6 ± 0.2	1.65 ± 0.02	2.7 ± 0.6	8.1 ± 0.6
1 h	O	4.7 ± 0.3	2.32 ± 0.01	2.7 ± 0.7	8.1 ± 0.6
	Ce	4.9 ± 0.3	3.83	1.2 ± 0.3	6.4 ± 0.5
	O	5.4 ± 1.0	4.55	1.2 ± 0.3	13.5 ± 0.8
2 h	O	0.7 ± 0.2	1.66 ± 0.02	3.6 ± 0.8	9.6 ± 0.8
	O	4.7 ± 0.3	2.33 ± 0.01	3.6 ± 0.8	9.6 ± 0.8
	Ce	4.5 ± 0.3	3.83	0.6 ± 0.4	6.8 ± 0.5
	O	5.7 ± 1.0	4.55	0.6 ± 0.4	15.3 ± 0.8
3 h	O	0.7 ± 0.2	1.67 ± 0.02	3.4 ± 0.8	8.0 ± 0.8
	O	5.0 ± 0.4	2.31 ± 0.01	3.4 ± 0.8	8.0 ± 0.8
	Ce	5.5 ± 0.4	3.83	2.0 ± 0.4	6.3 ± 0.5
	O	4.7 ± 1.1	4.55	2.0 ± 0.4	14.9 ± 1.1

Ceria nanorods			R	σ^2	ΔE_0
Reaction time	Atom	N	(Å)	(10^{-3} Å^2)	(eV)
5 h	O	0.7 ± 0.3	1.68 ± 0.03	6.1 ± 1.0	8.1 ± 1.0
	O	5.4 ± 0.6	2.32 ± 0.01	6.1 ± 1.0	8.1 ± 1.0
	Ce	5.0 ± 0.3	3.83	0.9 ± 0.4	6.6 ± 0.5
	O	3.8 ± 1.0	4.55	0.9 ± 0.4	15.3 ± 1.5
7 h	O	0.8 ± 0.3	1.68 ± 0.03	6.0 ± 1.0	9.6 ± 0.8
	O	5.4 ± 0.4	2.33 ± 0.01	6.0 ± 1.0	9.6 ± 0.8
	Ce	5.1 ± 0.4	3.83	2.0 ± 0.5	6.1 ± 0.4
	O	5.5 ± 1.1	4.55	2.0 ± 0.5	14.6 ± 1.0
10 h	O	0.7 ± 0.3	1.68 ± 0.03	6.6 ± 0.8	8.3 ± 0.6
	O	5.8 ± 0.4	2.33 ± 0.01	6.6 ± 0.8	8.3 ± 0.6
	Ce	4.9 ± 0.3	3.83	1.1 ± 0.4	5.5 ± 0.4
	O	5.7 ± 0.9	4.55	1.1 ± 0.4	13.8 ± 0.9

[a] The control sample is composed of ceria nanorods in 0.1 M Tris (pH = 7.54) buffer solution without any H_2O_2.

References

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