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Electronic Supplementary Information

Co-effects of UV/H_2O_2 and Natural Organic Matter on the Surface Chemistry of Cerium Oxide Nanoparticles

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Summary

16 pages, including experimental descriptions, 7 figures, and 8 tables.

S1. Characterization of CeO_2 nanoparticles

TEM Sample Preparation: Approximately 50 µL of the CeO_2 solution was placed onto 200-mesh Cu grids with Formvar-carbon films. After drying, the morphology and lattice spacing were determined using high resolution transmission electron microscopy (HRTEM, JEOL 2100F) with a 200 kV accelerating voltage. The lattice spacings closely matched those of CeO_2 nanoparticles.[1-2]

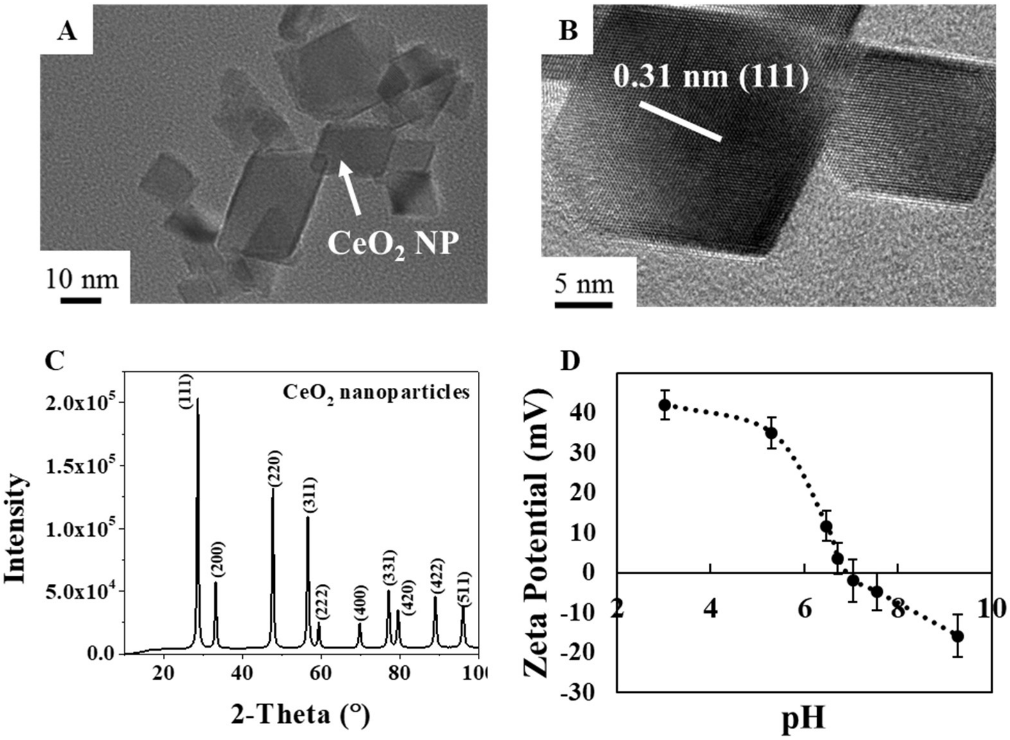

Fig. S1 (A) and (B): Representative TEM images and lattice spacing for unreacted CeO_2 NPs with 10 mM NaCl at pH 5.4. (C): Wide angle X-ray diffraction patterns of CeO_2 NPs taken at sector 11-ID-B of the Advanced Photon Source at Argonne National Laboratory. (D) Zeta potential of CeO_2 NPs in 10 mM NaCl at different pH values to determine the isoelectric point (i.e., ~ pH 6.9).

S2. NOM stock solution preparation.

Preparation of NOM Stock Solution: To create SRNOM stock solutions, 100 mg of NOM was added to 200 mL of DI water and stirred overnight in dark conditions (the bottle was wrapped in aluminum foil). The pH of the solution was then adjusted to 8.5 to increase the solubility before vacuum-filtering. This SRNOM stock solution was refrigerated prior to experimentation. Non-purgeable organic carbon (NPOC) concentrations in the stock solution were measured using a Shimadzu total organic carbon (TOC) Analyzer.

Table S1. Characterization of Suwannee River NOM provided by the International Humic Substances Society (IHSS).[3]

Carboxyl (meq/g C)	Phenolic (meq/g C)	Q_1	$LogK_1$	n_1	Q_2	$LogK_2$	n_2	N	RMSE
11.21	2.47	11.20	4.16	3.44	1.60	9.99	1.03	1705	0.1360
Source: Department of Chemistry, Environmental Sciences Ph.D. Program, Ball State University, Muncie, IN, U.S.A.									
$\mathbf{Q_1}$ and $\mathbf{Q_2}$ are the maximum charge densities of the two classes of binding sites **Log** $\mathbf{K_1}$ and **Log** $\mathbf{K_2}$ are the mean log K values for proton binding by the two classes of sites $\mathbf{n_1}$ and $\mathbf{n_2}$ are empirical parameters that control the width (in log K) of a class of proton binding sites									

S3. CeO_2 sedimentation experimental design.

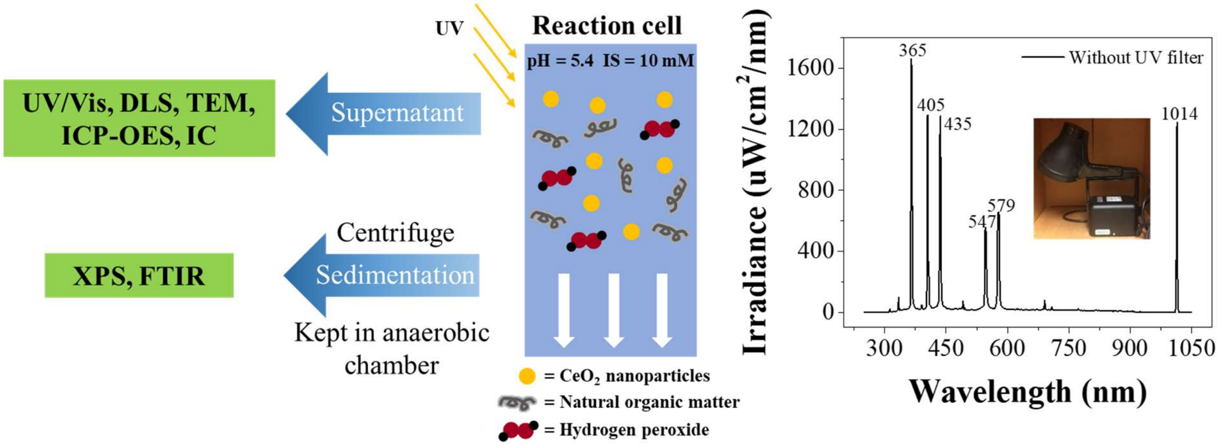

Fig. S2 Experimental procedures for UV-Vis, DLS, ICP-OES, TEM, XPS, and FTIR, and the irradiance spectrum of the UVA light source measured using a SpectrlLight 3. Suspended CeO_2 solutions at pH 5.4 were put into 50 mL test tubes and reacted for 2 hours. The ionic strength of the solutions was controlled at 10 mM using NaCl. At certain reaction times, 1 mL of supernatant was taken out to be measured using UV-Vis and DLS. After 2h reaction, the solutions were centrifuged for 15 minutes. The supernatant was taken out, leaving the sediment in the test tubes. The sediment was left to dry in an anaerobic chamber to prevent any further oxidation from air. XPS and FTIR were measured using the sedimentation as soon as it was dried.

Table S2. Detailed experimental conditions for UV-Vis experiments.

Conditions		**CeO_2 (mg/L)**	**H_2O_2 (mM)**	**NOM (mg C/L)**	**UV**	**pH**	**NaCl (mM)**
Light	H_2O_2	50	0/3/30	-	Yes	5.4 ± 0.1	10
	NOM	50	-	3.3 ± 0.2	Yes	5.4 ± 0.1	10
	H_2O_2 + NOM	50	3/30	3.3 ± 0.2	Yes	5.4 ± 0.1	10
Dark	H_2O_2	50	0/3/30	-	No	5.4 ± 0.1	10
	NOM	50	-	3.3 ± 0.2	No	5.4 ± 0.1	10
	H_2O_2 + NOM	50	3/30	3.3 ± 0.2	No	5.4 ± 0.1	10

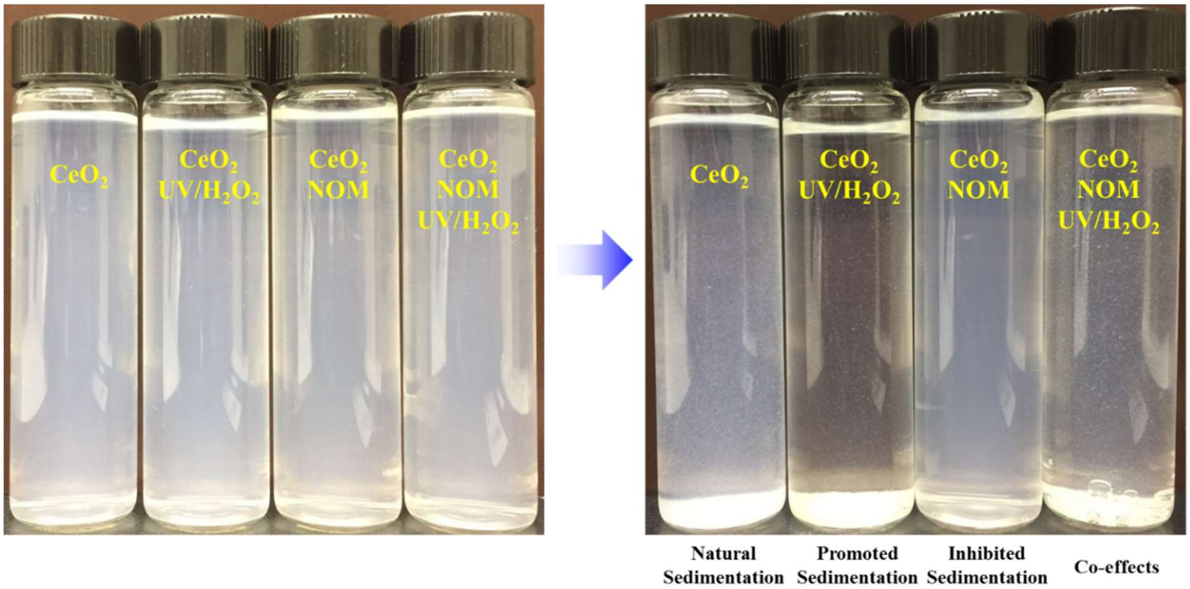

Fig. S3 Observed differences in the sedimentation of CeO_2 NPs in the presence of UV/H_2O_2 and/or NOM compared with the control experiment with 10 mM NaCl at pH 5.4 after 2 hrs reaction.

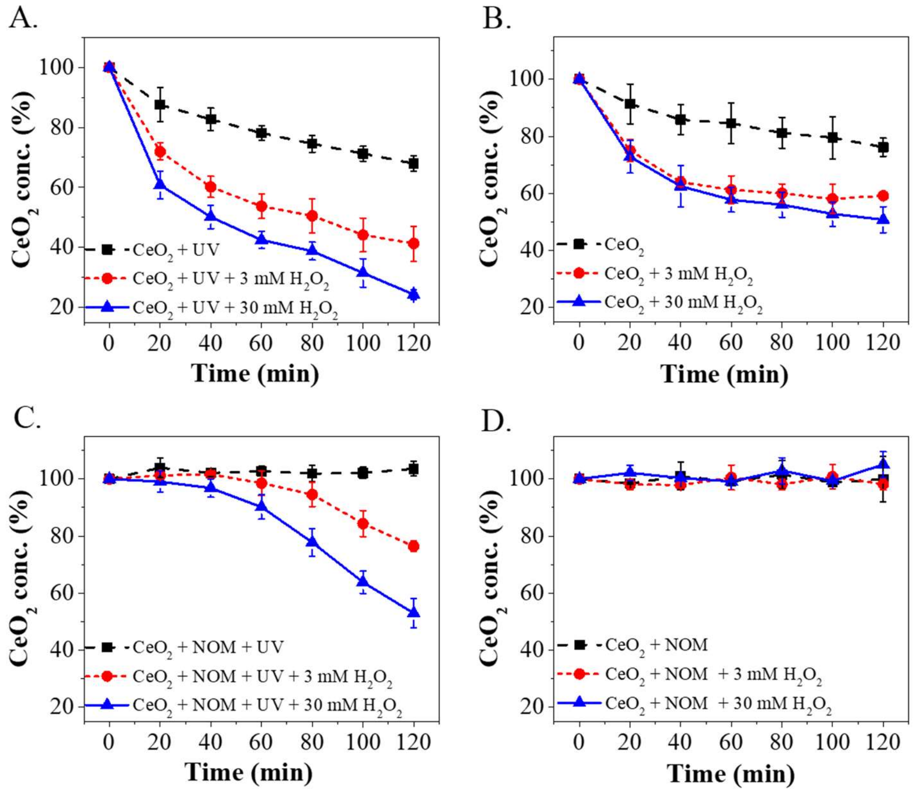

Fig. S4 UV-Vis data showing sedimentation of CeO_2 NPs with 10 mM NaCl at pH 5.4 in the presence and absence of UV/H_2O_2 and NOM: (A) CeO_2 with UV and H_2O_2. A higher concentration of H_2O_2 increased the extent of sedimentation; (B) CeO_2 with H_2O_2. H_2O_2 alone showed destabilizing effects on CeO_2; (C) CeO_2 with NOM, UV, and H_2O_2. With a higher concentration of H_2O_2, CeO_2 started to settle in a shorter time range; and (D) CeO_2 with NOM and H_2O_2. NOM concentration was quantified as 3.3 ± 0.2 mg C/L by NPOC. The percentages were obtained by normalizing the suspended nanoparticle concentration by the initial suspended concentration measured using UV-Vis. The error bars represent the standard deviation of CeO_2 NP concentrations from triplicate experiments.

Table S3. Zeta potential and hydrodynamic particle size values for CeO_2 NPs with 10 mM NaCl at pH 5.4 in the presence and absence of UV/H_2O_2 and NOM. The initial CeO_2 NPs concentration was 50 mg/L, and the NOM concentration was 3.3 ± 0.2 mg C/L. The zeta potential for stable dispersions of unreacted CeO_2 in DI water at pH 5.4 was 39.2 ± 3.4 mV. The hydrodynamic particle size was 140.7 ± 53.0 nm for stable dispersions of unreacted CeO_2 in DI water at pH 5.4.

Conditions	**Zeta potential (mV)**		**Z-Ave (d. nm)**	
	1 hr	**2 hrs**	**1 hr**	**2 hrs**
CeO_2	39.5 ± 2.6	38.6 ± 5.1	256.0 ± 49.0	460.0 ± 60.1
CeO_2 + UV	38.8 ± 4.2	35.0 ± 4.6	275.0 ± 59.9	513.0 ± 74.0
CeO_2 + 30 mM H_2O_2	32.0 ± 4.5	30.9 ± 3.3	1983.0 ± 132.1	2706.0 ± 145.4
CeO_2 + UV + 30 mM H_2O_2	5.4 ± 3.8	3.8 ± 3.4	3954.0 ± 171.8	5574.0 ± 252.8
CeO_2 + NOM	-43.9 ± 6.9	-38.3 ± 1.8	153.0 ± 35.5	174.7 ± 38.5
CeO_2 + NOM + UV	-40.8 ± 4.6	-36.4 ± 1.7	172.3 ± 34.5	182.0 ± 39.2
CeO_2 + NOM + 30 mM H_2O_2	-39.5 ± 5.2	-36.2 ± 1.1	173.9 ± 30.9	183.9 ± 39.3
CeO_2 + NOM + UV + 30 mM H_2O_2	-38.9 ± 5.6	-12.9 ± 2.1	250.6 ± 41.4	3276.0 ± 122.3

Table S4. pH measurements of the reaction and control systems for CeO_2 NPs at 10 mM NaCl and an initial pH of 5.4.

Conditions	Starting pH values	Final pH values (2h)
CeO_2	5.4 ± 0.1	5.7 ± 0.1
CeO_2 + UV	5.4 ± 0.1	5.6 ± 0.1
CeO_2 + 3 mM H_2O_2	5.4 ± 0.1	5.3 ± 0.1
CeO_2 + 30 mM H_2O_2	5.4 ± 0.1	5.3 ± 0.1
CeO_2 + UV + 3 mM H_2O_2	5.4 ± 0.1	5.3 ± 0.1
CeO_2 + UV + 30 mM H_2O_2	5.4 ± 0.1	5.1 ± 0.1
CeO_2 + NOM	5.4 ± 0.1	5.1 ± 0.1
CeO_2 + NOM + UV	5.4 ± 0.1	4.9 ± 0.1
CeO_2 + NOM + 3 mM H_2O_2	5.4 ± 0.1	4.9 ± 0.1
CeO_2 + NOM + 30 mM H_2O_2	5.4 ± 0.1	4.9 ± 0.1
CeO_2 + NOM + UV + 3 mM H_2O_2	5.4 ± 0.1	4.7 ± 0.1
CeO_2 + NOM + UV + 30 mM H_2O_2	5.4 ± 0.1	4.6 ± 0.1

CeO_2 nanoparticle dissolution tests using inductively coupled plasma optical emission spectrometry (ICP-OES): Due to the low solubility of CeO_2, 250 mg/L CeO_2 suspensions and 150 mM H_2O_2 were used in order to achieve aqueous Ce concentrations higher than the detection limit of ICP-OES (25 μg/L). Because the concentrations of CeO_2 and H_2O_2 were scaled up by the same multiples, this elevated concentration system is relevant to lower concentration systems. Reactions were prepared as described for sedimentation experiments. At 1 hr and 2 hrs, triplicate samples were placed in ultracentrifuge tubes (PC Oak Ridge Tubes, Fisher Scientific) and ultracentrifuged using a Thermo Scientific Sorvall WX Ultra Series Centrifuge with a T865 Fixed Angle Rotor at 40,000 rpm (or 115,861g) for 30 min. After ultracentrifuging, samples were filtered using a 0.2 µm polypropylene filter (Millipore syringe filter) to ensure the removal of all bulk CeO_2 NPs and aggregates. The filtrate was collected and acidified to 1% v/v nitric acid for ICP-OES measurements. This method was also used in our previous studies and other CeO_2 NP dissolution studies.[4-5] From the results (Table S2), UV/H_2O_2 exposure did not promote CeO_2 NP dissolution compared with the control system.

Table S5. Dissolved Ce concentrations (µg/L) in NaCl systems in the presence of UV and H_2O_2 at pH 5.4, measured by ICP-OES. Std. Dev., standard deviation with 95% confidence level.

System	1 hr	Std. Dev.	2 hrs	Std. Dev.
CeO_2 + NaCl + UV + H_2O_2	11.9	2.3	6.4	3.2
CeO_2 + NaCl + UV	17.7	4.7	20.6	21.6
CeO_2 + NaCl + H_2O_2	26.6	4.4	23.9	6.1
CeO_2 + NaCl	18.6	5.2	39.7	14.8

NOM decomposition measurement using ion chromatography (IC): Reactions were prepared as described for sedimentation experiments. At 0, 20, 40, 60, 80, 100, and 120 minutes, triplicate samples were filtered using a 0.2 µm polypropylene filter (Millipore syringe filter). Both formate and acetate were measured, but only acetate was detected during the reaction.

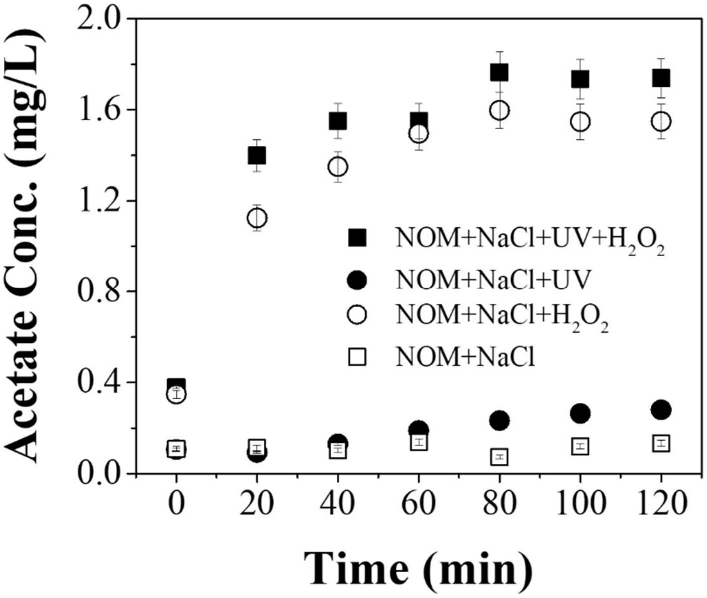

Fig. S5 Measurement of acetate produced from the decomposition of NOM during the reaction with CeO_2 and UV/H_2O_2 exposure using ion chromatography (IC).

S4. XPS reference

Table S6. XPS reference binding energies, absolute values of areas for each peak, and calculated percentages of Ce^{3+} at different conditions for Ce 3d.

	U''	U'	U	V'''	V''	V'	V	
BE (eV)	907.20	903.50	900.60	897.90	888.30	885.0	881.90	Ce^{3+}%
	Ce^{4+}	Ce^{3+}	Ce^{4+}	Ce^{4+}	Ce^{4+}	Ce^{3+}	Ce^{4+}	
CeO_2 control	1708	1614	2762	6150	4992	2797	4730	17.8%
CeO_2 + UV/H_2O_2	8524	15094	11555	22697	16731	16128	19459	28.3%
CeO_2 + NOM	2907	3234	3498	7190	5238	2361	6671	18.0%
CeO_2 + NOM + UV/H_2O_2	3139	5960	11753	16325	11326	11179	18904	21.8%

Table S7. XPS reference binding energies, absolute values of areas for each peak, and calculated percentages of each corresponding bond at different conditions for C 1s.

Area and percentages	C 1s			
	C-C (284.8 eV)	C=O (285.6 eV)	O-C=O (288.8 eV)	Total of C=O and O-C=O
CeO_2 control	6427 86.0%	653 8.7%	396 5.3%	1049 14.0%
CeO_2 + UV/H_2O_2	14828 78.2%	1985 10.5%	2140 11.3%	4125 21.8%
CeO_2 + NOM	10786 63.7%	4203 24.8%	1951 11.5%	6154 36.3%
CeO_2 + NOM + UV/H_2O_2	15586 77.0%	3027 14.9%	1642 8.1%	4669 23.0%

Table S8. XPS reference binding energies, absolute values of areas for each peak, and calculated percentages of each corresponding bond at different conditions for O 1s.

Area and percentages	O 1s			
	O_I	O_{II}	O_{III}	O_{IV}
	Lattice oxygen (528.9 eV)	Superposition of CO_3^{2-} and $O_2^{\cdot-}$ (530.1 eV)	Hydroxyl-like groups (531.8 eV)	Residual adsorbed H_2O (534.1 eV)
CeO_2 control	8942 51.6%	1988 11.5%	5188 29.9%	1221 7.0%
CeO_2 + UV/H_2O_2	5799 32.6%	6545 36.8%	4662 26.2%	765 4.3%
CeO_2 + UV/H_2O_2 + t-ButOH	5628 31.1%	8675 48.0%	2709 15.0%	1058 5.9%
CeO_2 + UV/H_2O_2 + SOD	8176 53.9%	2759 18.2%	3738 24.6%	506 3.3%

S5. FTIR spectrum of unreacted CeO_2 NPs

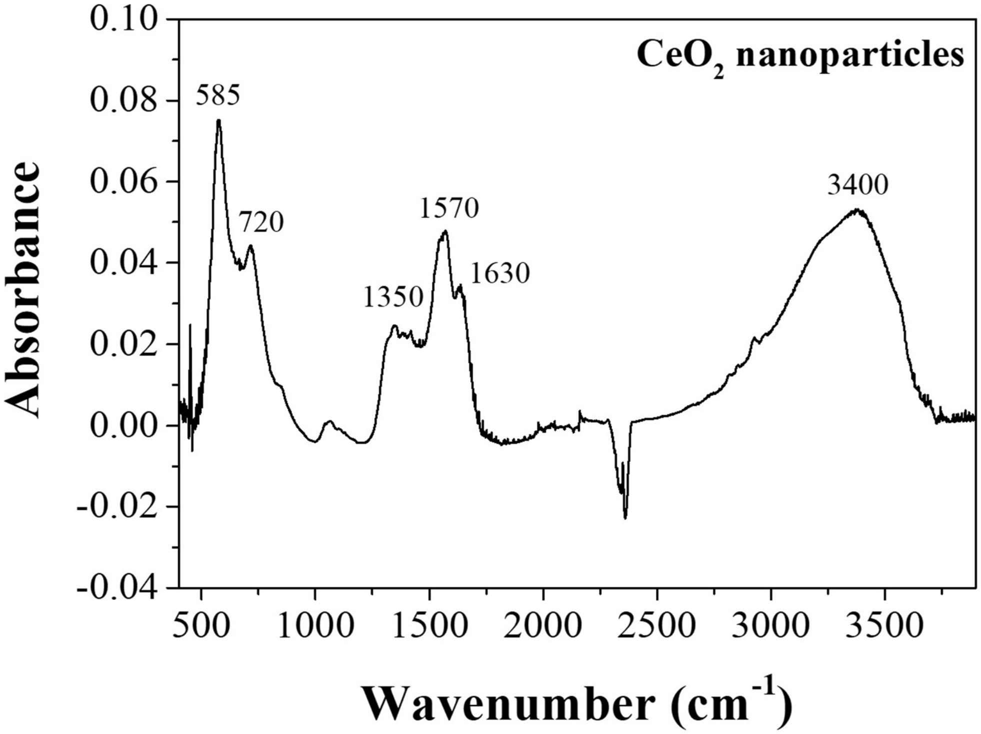

Fig. S6 FTIR spectrum of unreacted CeO_2 NPs.

S6. Contact angles of DI water on CeO_2-sputtered Si wafers under different conditions

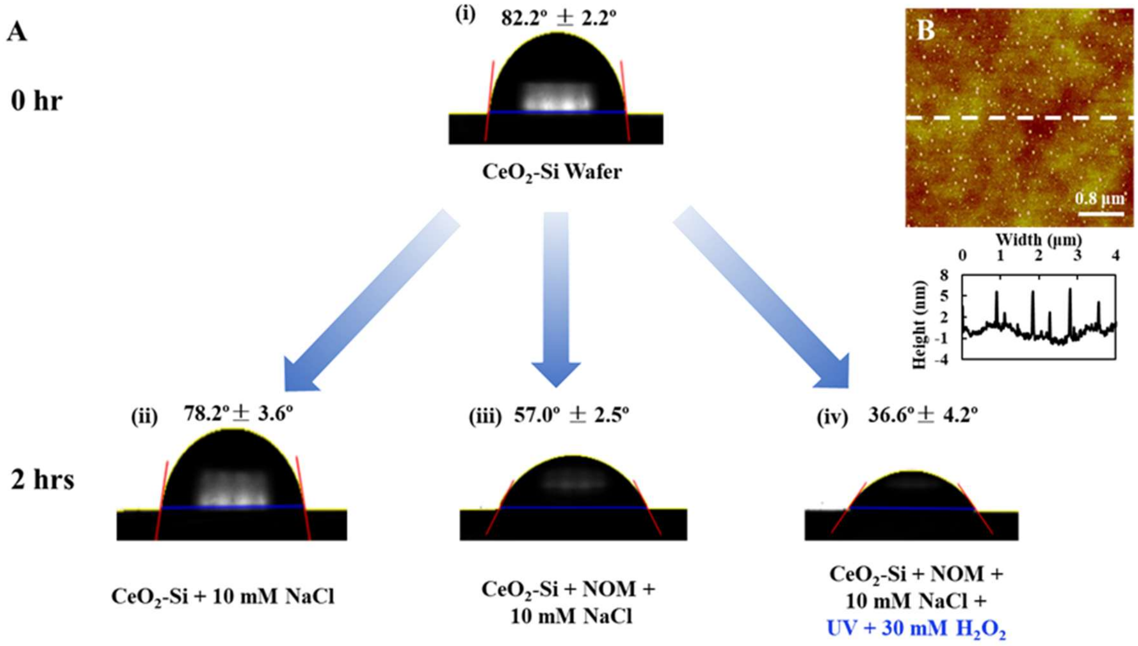

Fig. S7 Measurements of contact angles for CeO_2-sputtered Si wafers at 10 mM IS and pH 5.4. **A**: contact angles of (i) unreacted CeO_2-Si wafer at 0 hr, (ii) CeO_2-sputtered Si wafer with NaCl solution at 2 hrs, (iii) CeO_2-sputtered Si wafer with 10 mM NaCl and 3.3 mg C/L NOM at 2 hrs, (iv) CeO_2-sputtered Si wafer with 10 mM NaCl, 3.3 ± 0.2 mg C/L NOM, UV, and 30 mM H_2O_2 at 2 hrs. **B**: Atomic force microscopy (AFM) image (4 μm × 4 μm) of an unreacted CeO_2-sputtered Si wafer surface. For each experimental condition, a 5 mm × 5 mm CeO_2-sputtered Si wafer piece was cut from a larger CeO_2-sputtered Si wafer to be used.

References

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