Almost Complete Removal of Sub-90 nm Ceria Particles from Silicon Dioxide Surfaces

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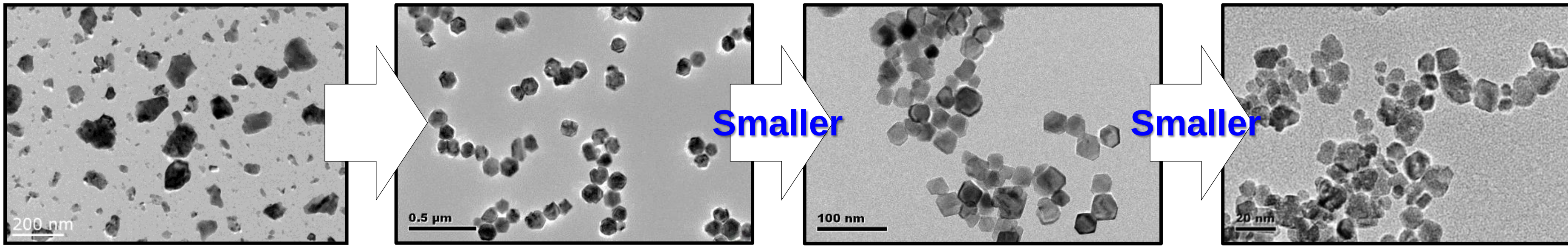
Trends of Ceria Slurries

Calcined Ceria **Colloidal Ceria**



median size ~110nm | median size ~90nm | median size ~30nm | median size ~10nm

- **High SiO_2 removal rate**
- **High crystallinity**
- **Tunable particle size**
- **Mass production**
- **Facet shape**
- **Poor size distribution**
- **Relatively high scratch**

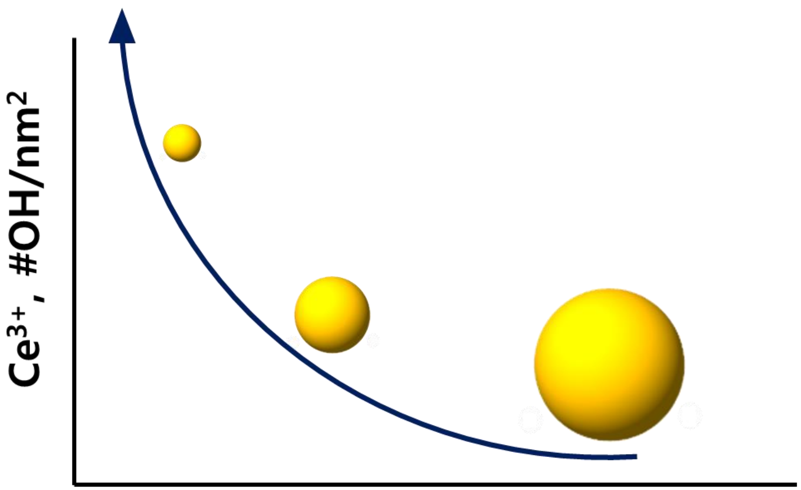
→

- **Uniform size distribution**
- **Spherical shape**
- **Low scratch**
- **High cost**
- **Relatively Low SiO_2 RR**

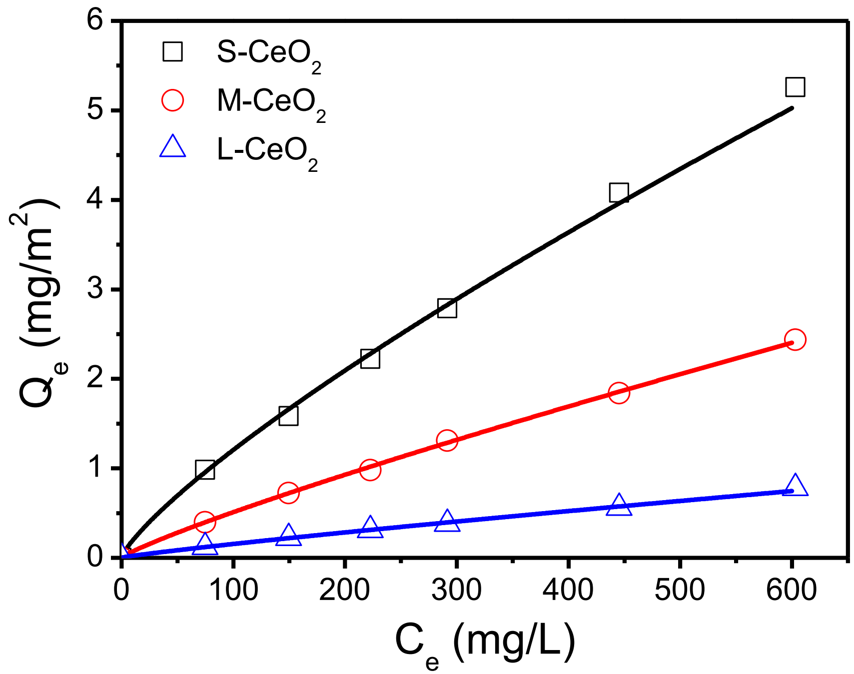
J. Seo,et al., *ACS Appl Mater Inter*, 2014, 6, 7388-7394.
J. Seo, in *21st International Symposium on Chemical-Mechanical Planarization*, Lake Placid, NY, USA, 2017.

Interaction between Ceria particle and SiO_2 surface

Size-dependent surface chemistry of ceria



Adsorption of silicate ion on ceria surface



	Adsorption constant		
	K_F	1/n	R^2
$S\text{-}CeO_2$	0.0570	0.6771	0.9646
$M\text{-}CeO_2$	0.0207	0.7135	0.9639
$L\text{-}CeO_2$	0.0048	0.7650	0.9797

J. Seo,et al.,*Applied Surface Science*, 2016, 389, 311-315.

Traditional Cleaning Solutions

1. **Piranha (98% H_2SO_4 : 30% H_2O_2 - 4 : 1) at 90 ~ 120 °C**

   –Removal of organic contaminants

2. **SC-1 (29% NH_4OH : 30% H_2O_2 : H_2O – 1 : 1 : 5) at 80 ~ 90°C**

   –Removal of particles and organic contaminants

3. **SC-2 (37% HCl : 30% H_2O_2 : H_2O – 1 : 1 : 5) at 80 ~ 90 °C**

   –Removal of metallic contaminants

4. **DHF (dilute HF, typically less than 0.5 vol% of 47% HF) at 25 ℃**

   –Removal of a thin oxide layer

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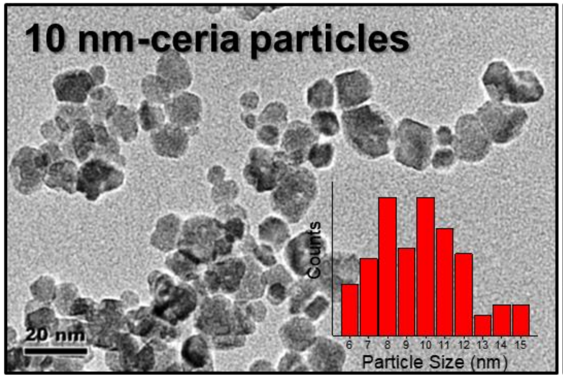
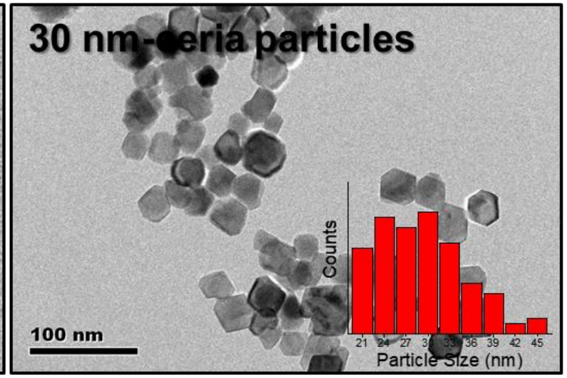
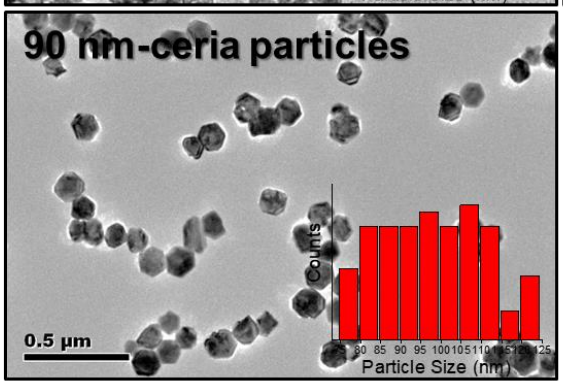
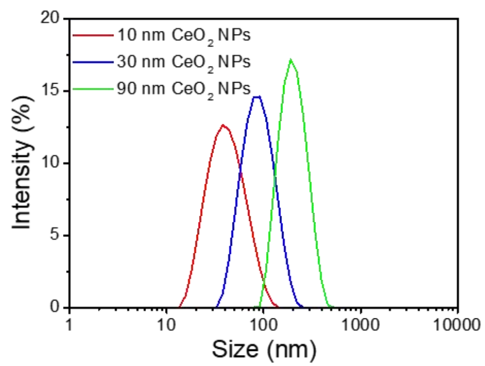
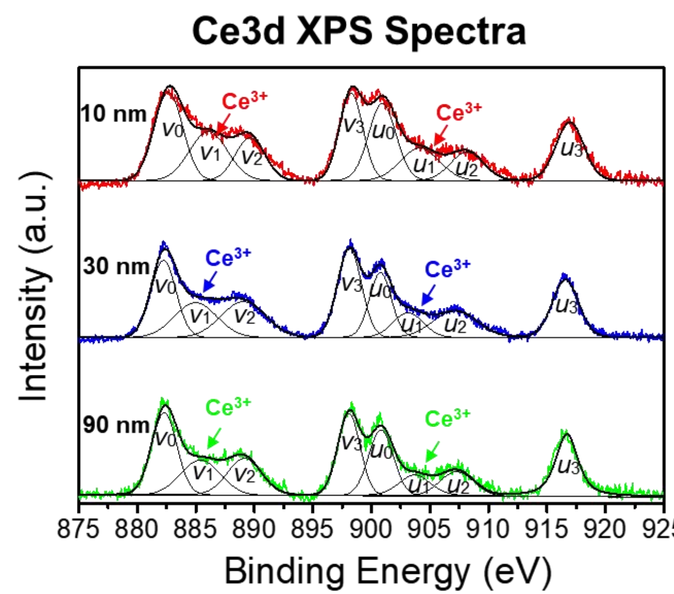
Physico-chemical properties of ceria particles with different sizes











	S_{BET} (m^2/g)	d_{BET}[a] (nm)	d_{TEM}[b] (nm)	d_{DLS}[c] (nm)	Ce^{3+} (%)
10 nm-ceria	84.3	10 nm	10 nm	36 nm	26.3 %
30 nm-ceria	28.8	29 nm	29 nm	81 nm	18.4 %
90 nm-ceria	8.0	98 nm	104 nm	193 nm	15.0 %

Table. Physicochemical properties of ceria particles with different sizes.
[a]Obtained from Solvay. [b]Calculated from TEM image. [c]Measured using DLS method

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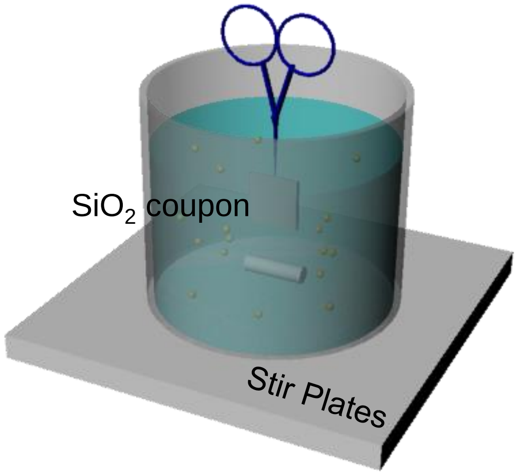
Our lab-based evaluation method for cleaning study

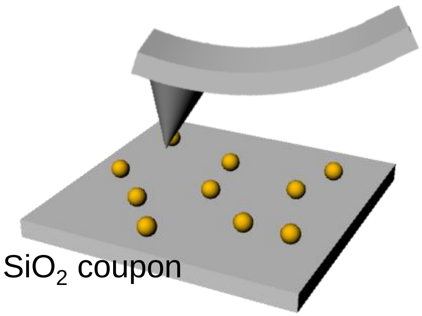
1st) Preparation of contaminated coupon



Slurry
· CeO_2 0.05 wt%
· Volume: 100 mL

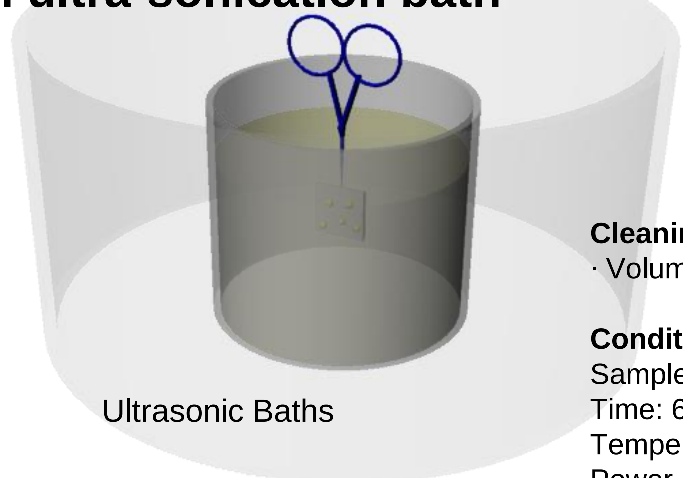
Conditions
Sample size: 1 x 1 cm^2
Time: 60s @ 300 rpm
Temperature : 25 ^oC

DIW rinsing



AFM measurements
· Park Systems (XE-300P)
· Non-Contact with NCHR
· Scan rate 0.5 Hz

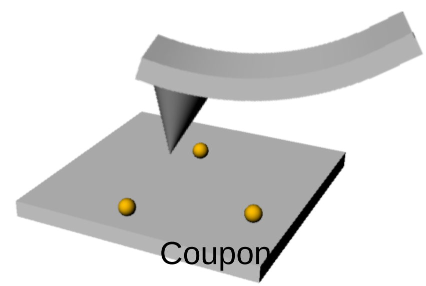
2nd) Cleaning with our solutions in ultra-sonication bath



Cleaning solutions
· Volume: 100 mL

Conditions
Sample size: 1 x 1 cm^2
Time: 60s
Temperature : 25 ^oC
Power : 75 W, Frequency: ~40 kHz

DIW rinsing



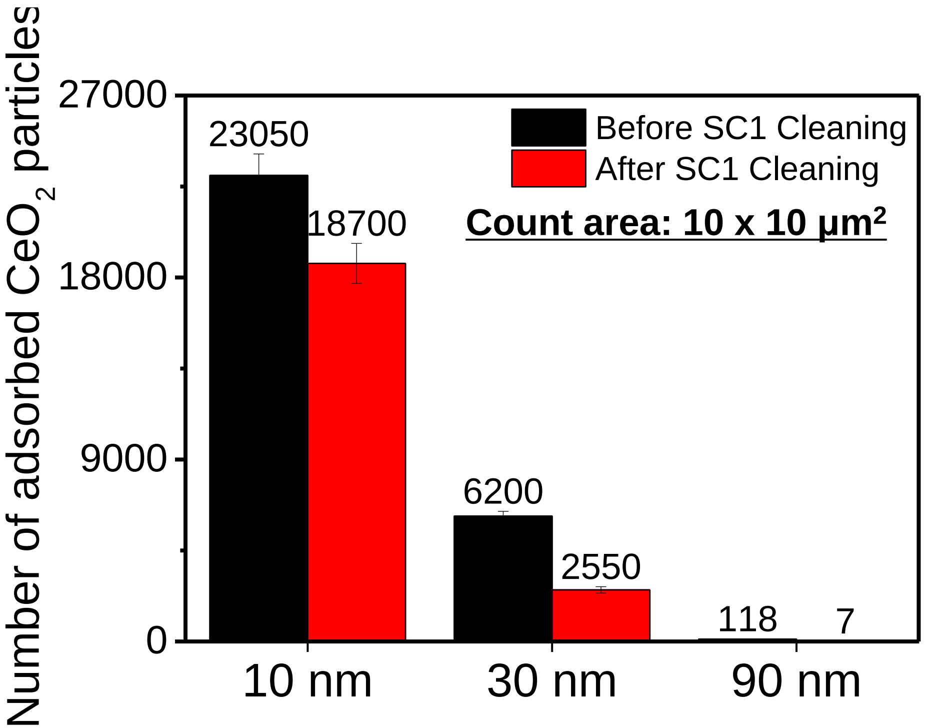
Cleaning efficiencies (CE)

$$= \frac{\text{Particle (initial)} - \text{Particle (residual)}}{\text{Particle (initial)}}$$

Size-dependent Cleaning Efficiency

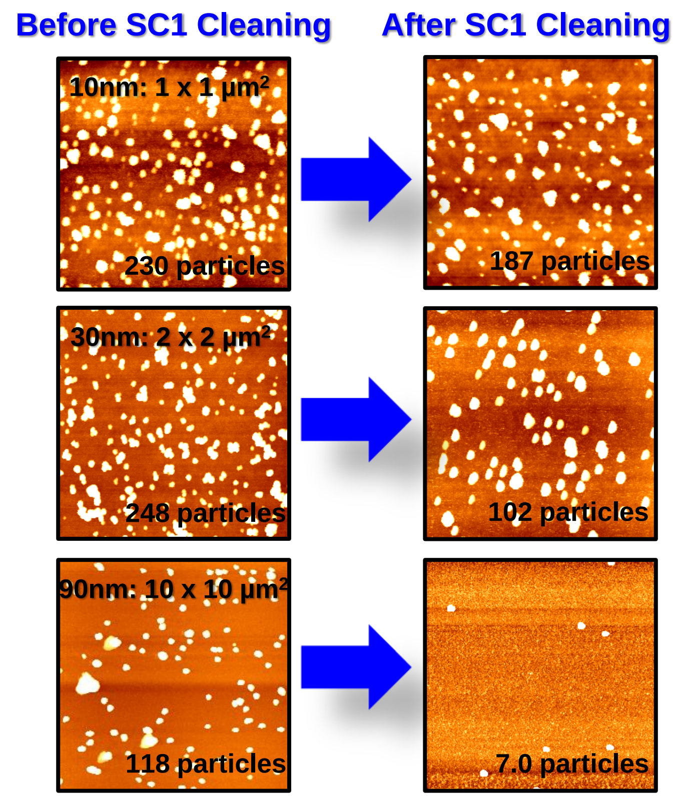
SC1 solution consisting of 1:1:5 (v/v/v) mixture of NH_4OH (30 wt%)/H_2O_2 (30 wt%)/DIW

Number of ceria particles before and after SC1 Cleaning



	10 nm	30 nm	90 nm
Cleaning Efficiency	19 %	58 %	94 %

$$\text{Cleaning Efficiency (CE)}: \frac{CeO_2\text{ (initial)} - CeO_2\text{ (residual)}}{CeO_2\text{ (initial)}} \times 100$$



Number of ceria particles in scan area

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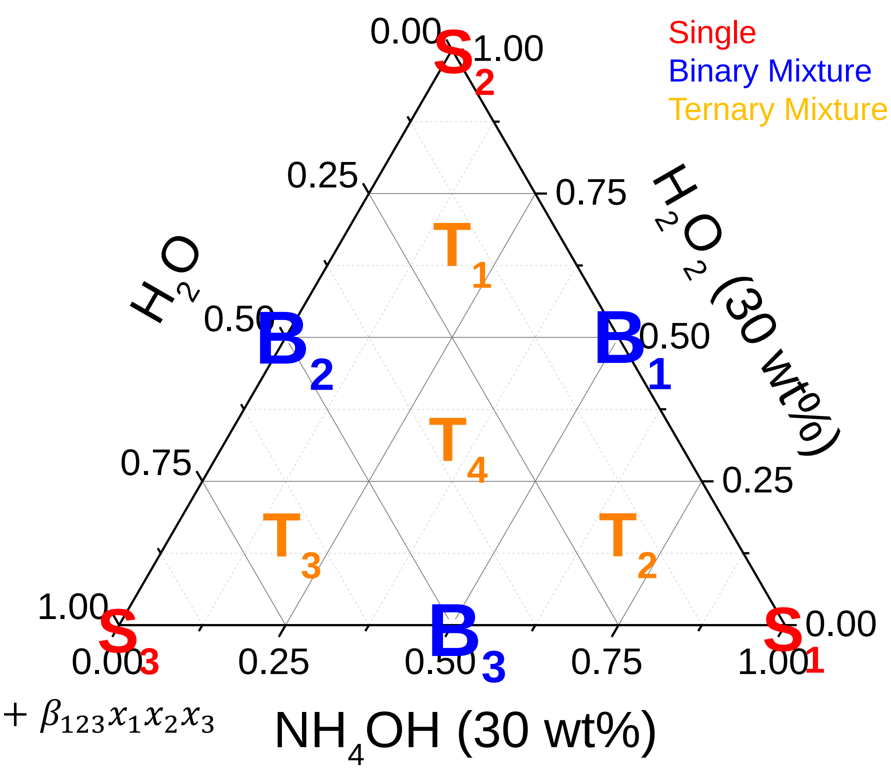
H_2O_2-NH_4OH mixtures and Their Optimization

Design of experiments (DOE)

Volume % mixture

Sample Number	H_2O_2	NH_4OH	DIW
1	100	0	0
2	0	100	0
3	0	0	100
4	50	50	0
5	50	0	50
6	0	50	50
7	66.67	16.67	16.67
8	16.67	66.67	16.67
9	16.67	16.67	66.67
10	33.3	33.3	33.3

Augmented simplex-centroid design used to optimize composition of H_2O_2-NH_4OH mixtures



Fitting model,

$$Y = \sum_{i=1}^{3} \beta_i x_i + \sum\sum_{i<j}^{3} \beta_{ij} x_i x_j + \sum\sum_{i<j}^{3} \delta_{ij} \beta_{ij} x_i x_j (x_i - x_j) + \beta_{123} x_1 x_2 x_3$$

x_1 (30 wt% H_2O_2), x_2 (30 wt% NH_4OH) and x_3 (H_2O)

Logit transformation $Y = \ln(y/(1-y))$

where y is the cleaning efficiency expressed in the range of 0 to 1.

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H_2O_2-NH_4OH mixtures and Their Optimization

Summary of Optimization of H_2O_2-based Alkaline Solutions

Solution Number	H_2O_2 (30 wt%)	NH_4OH (30 wt%)	DIW	pH	Rq (nm)	Cleaning Efficiency		
						10 nm	30 nm	90 nm
1	100	0	0	4.5	0.6	<5 %	<5 %	<5 %
2	0	100	0	13.7	0.9	19 %	23 %	60 %
3	0	0	100	6.0	0.6	<5.0 %	<5.0 %	<5 %
4	50	50	0	13.2	0.8	98 %	99 %	99 %
5	50	0	50	4.7	0.6	<5 %	<5 %	<5 %
6	0	50	50	13.5	0.8	<5 %	<5 %	<5 %
7	66.66	16.67	16.67	12.5	0.7	28 %	56 %	89 %
8	16.67	66.66	16.67	13.4	0.7	27 %	62 %	89 %
9	16.67	16.67	66.66	12.8	0.7	31 %	68 %	90 %
10	33.3	33.3	33.3	12.9	0.8	43 %	89 %	99 %
SC1	14.3	14.3	71.4	12.0	0.7	19 %	58 %	94 %

Table. Surface roughness (Rq) and cleaning efficiencies of the ten compositions tested based on full cubic model, and SC1 solution.

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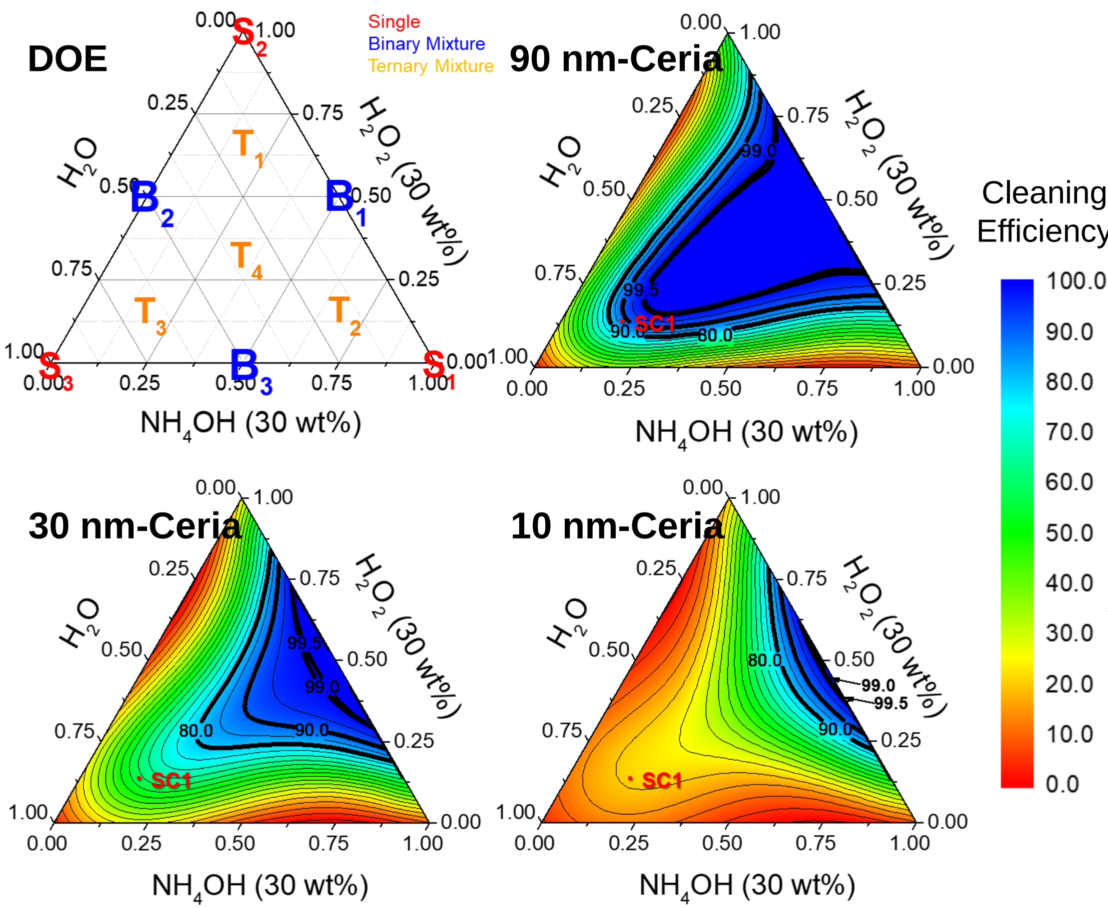
H_2O_2-NH_4OH mixtures and Their Optimization

Summary of Optimization of H_2O_2-NH_4OH mixtures



Cleaning efficiencies of SC1 solution

	Experimental	Predicted
10 nm	19 %	23 %
30 nm	58 %	61 %
90 nm	94 %	90 %

$$Y_{90nm} = -2.9x_1 + 0.4x_2 - 2.9x_3 + 24.5x_1x_2 - 0.04x_1x_3 - 6.7x_2x_3 + 145.1x_1x_2(x_1 - x_2) + 7.8x_1x_3(x_1 - x_3) - 21.8x_2x_3(x_2 - x_3) - 26.2x_1x_2x_3$$

$$Y_{30nm} = -2.9x_1 - 1.2x_2 - 2.9x_3 + 30.3x_1x_2 - 0.04x_1x_3 - 0.03x_2x_3 - 3.5x_1x_2(x_1 - x_2) - 37.7x_1x_3(x_1 - x_3) - 19.8x_2x_3(x_2 - x_3) - 20.8x_1x_2x_3$$

$$Y_{10nm} = -3.0x_1 - 1.5x_2 - 3.0x_3 + 25.1x_1x_2 - 0.1x_1x_3 - 3.0x_2x_3 - 12.5x_1x_2(x_1 - x_2) - 3.9x_1x_3(x_1 - x_3) - 11.8x_2x_3(x_2 - x_3) - 13.7x_1x_2x_3$$

A contour plot of cleaning efficiencies showing the synergistic effect of H_2O_2 (30 wt%), NH_4OH (30 wt%), and H_2O mixtures; 90 nm-ceria, 30 nm-ceria, and 10 nm-ceria..

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Perhydroxyl ion concentration

$$\mathbf{H_2O_2 + OH^- \overset{K_{eq}}{\longleftrightarrow} HO_2^- + H_2O}$$

$pK_a = 11.6$

where $K_{eq} = \frac{[HO_2^-]}{[HO^-][H_2O_2]} = \frac{K_{ion}}{K_W}$

$K_{ion} = \frac{[H^+][HO_2^-]}{[H_2O_2]}$ (2.24×10^{-12} mol/L at 25 °C) for H_2O_2

K_W for water is 1.0×10^{-14} mol^2/L^2 at 25 °C

X = starting molar concentration of NH_4OH

Y = starting molar concentration of H_2O_2

Z = formed molar concentration of $[HO_2^-]$ at equilibrium

$[HO^-]$ and $[H_2O_2]$ are the concentrations of hydroxyl ion and undecomposed hydrogen peroxide at equilibrium, respectively, which gives $[HO^-] = X - Z$ and $[H_2O_2] = Y - Z$

$$K_{eq} = \frac{[HO_2^-]}{[HO^-][H_2O_2]} = \frac{Z}{(X-Z)(Y-Z)}$$

$$[\mathbf{HO_2^-}] = \frac{\mathbf{R - \sqrt{R^2 - 4XY}}}{\mathbf{2}}$$

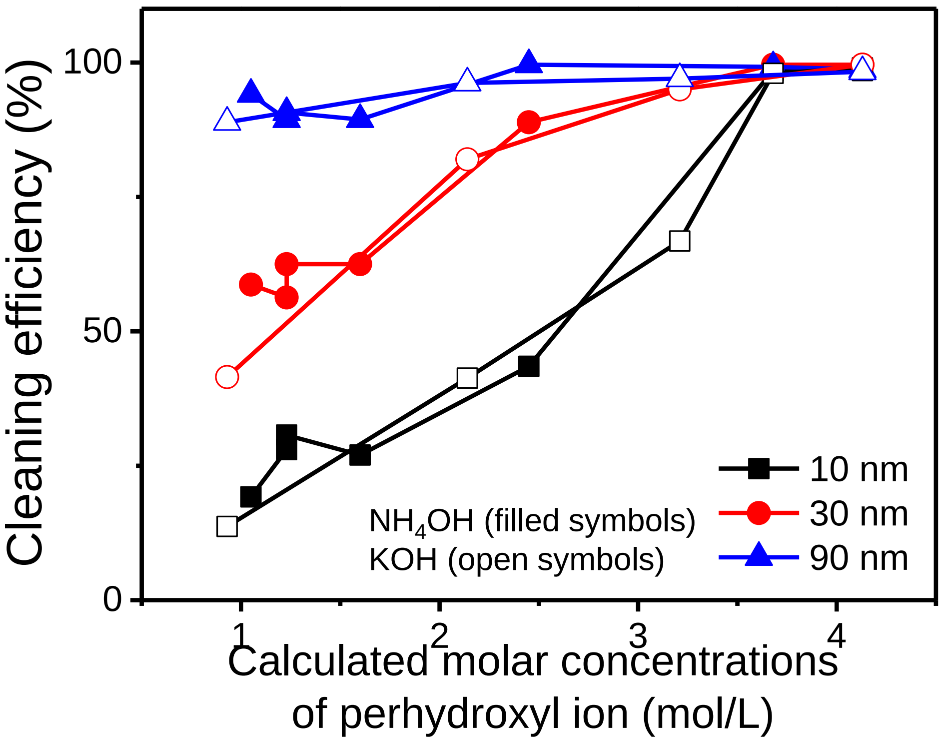
where $R = X + Y + 1/K_{eq}$

$[HO_2^-]$ has a maximum when $R^2 = 4XY$

Maximum value of $[HO_2^-] = X = Y$

Calculated molar concentration of perhydroxyl anion of cleaning solutions and their cleaning efficiencies

Cleaning efficiency as a function of perhydroxyl ions in mixtures of H_2O_2-based alkaline cleaning solution



Solution Number	Perhydroxyl Ions (mol/L)	Cleaning Efficiency		
		10 nm	30 nm	90 nm
1	0.00	<5 %	<5 %	<5 %
2	0.00	19 %	23 %	60 %
3	0.00	<5.0 %	<5.0 %	<5 %
4	3.68	98 %	99 %	99 %
5	0.00	<5 %	<5 %	<5 %
6	0.00	<5 %	<5 %	<5 %
7	1.23	28 %	56 %	89 %
8	1.60	27 %	62 %	89 %
9	1.23	31 %	68 %	90 %
10	2.45	43 %	89 %	99 %
SC1	1.05	19 %	58 %	94 %
NH_4OH-1	4.13	99 %	99 %	99 %
KOH-1	3.26	67 %	95 %	97 %
KOH-2	2.17	41 %	82 %	96 %
KOH-3	0.93	14 %	41 %	89 %
KOH-4	4.13	98 %	99 %	98 %

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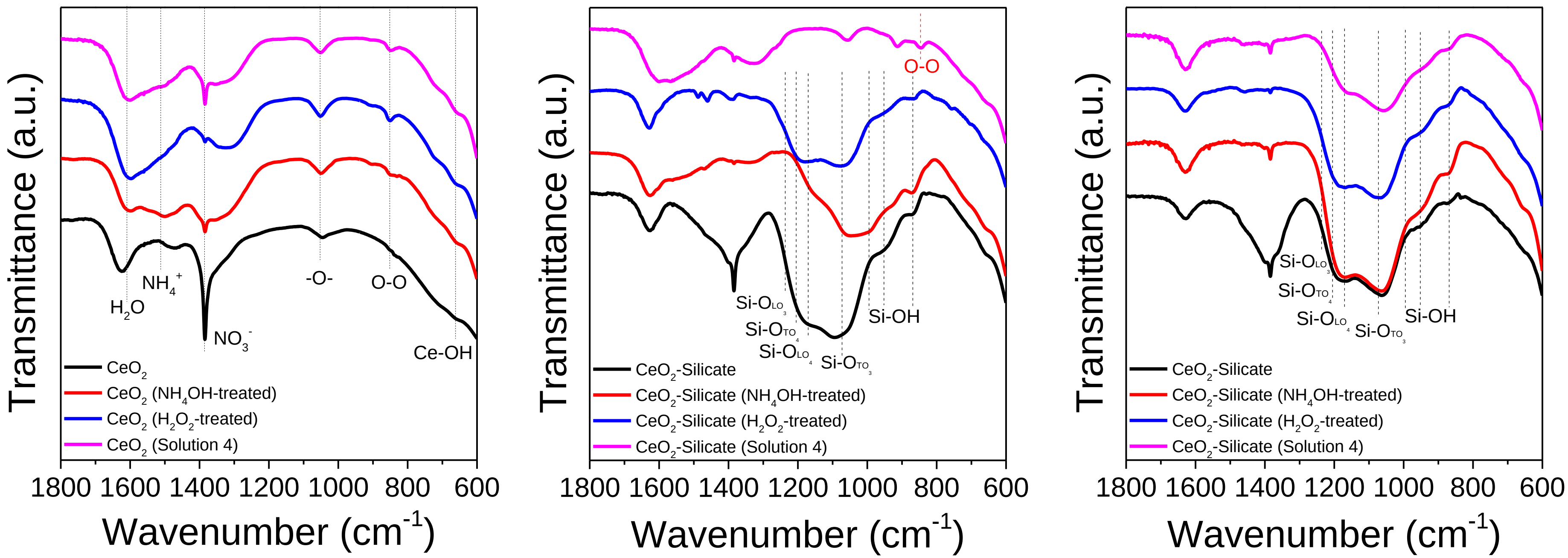
Cleaning mechanism in H_2O_2-based alkaline solutions and breakage of Ce-O-Si bonds

As-received CeO_2 | **Silicate-covered CeO_2 (partially covered)** | **Silicate-covered CeO_2 (more concentrated silicate)**



FT-IR spectra of ceria particles in the region of 1800-600 cm^{-1}. As-received, silicate (0.01 wt%) silicate (0.1 wt%) covered 10 nm-ceria particles that were reacted with four different solutions (H_2O, H_2O_2 (30 wt%), NH_4OH (30 wt%), and H_2O_2-NH_4OH mixture (50/50 volume ratios).

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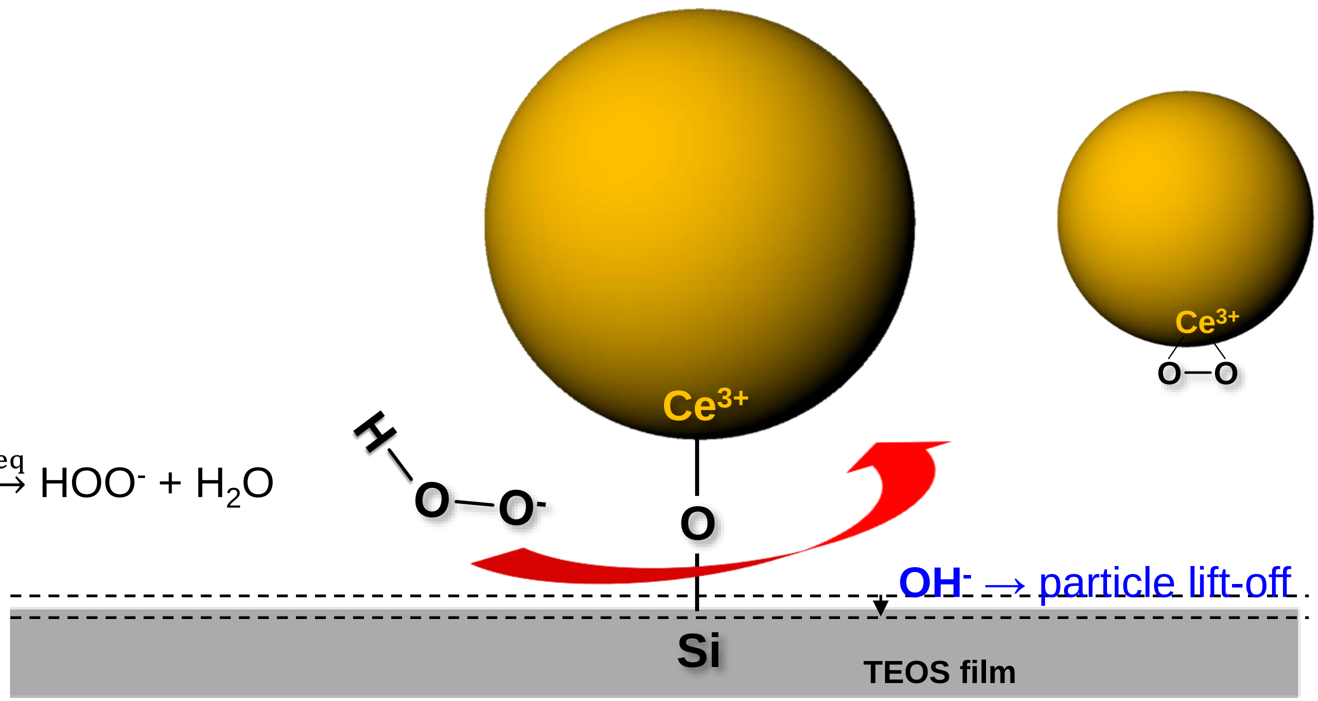
Schematic illustration of the removal of ceria particles by H_2O_2-based alkaline cleaning solution

$$H_2O_2 + OH^- \overset{K_{eq}}{\longleftrightarrow} HOO^- + H_2O$$



Bond type		Bond dissociation energy (kJ/mol)
Perhydroxyl anion (OOH)	O-O	210
	O-H	336
Hydroxyl ion	O-H	487
Ce-O-Si	Ce-O	790
	Si-O	452

Table. Known binding energy data

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Summary

Smaller ceria particles are more difficult to remove from oxide surfaces after CMP.

We showed that high pH H_2O_2-based cleaning solutions, aided by ultrasonic energy, can almost completely remove ceria particles down to 10 nm in size as determined by AFM imaging and counting.

Highest removal efficiencies were obtained when the molar concentration of the perhydroxyl ions [HO_2^-] is the highest possible in the cleaning solution.

Acknowledgement

1. Dr. S.V. Babu
2. Ebara Corporation
3. Solvay