Towards Understanding Smaller Ceria Particles (< 10 nm) for SiO_2 Removal during CMP

Ravitej Venkataswamy[1], Ngoc-Tram Le[1], Kyungju Park[2], Hyungoo Kang[2], Sungwon Park[1], Lyle Trimble[1], and Jihoon Seo[1]

[1]*Chemical & Biomolecular Engineering & Center for Advanced Materials Processing, Clarkson University*

[2]C&C Materials Development, SK Hynix Inc., Icheon-si, South Korea.

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CAMP Center for Advanced Materials Processing

I. Introduction and motivation

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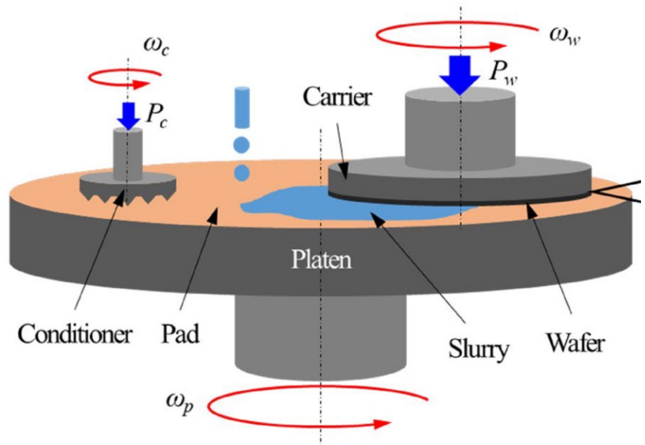
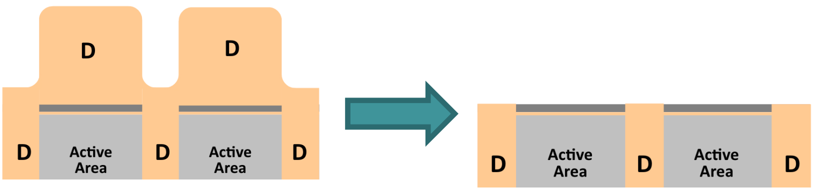
Chemical Mechanical Planarization



- CMP Process is widely used for local and global planarization of wafer in semiconductor manufact uring

STI CMP Process



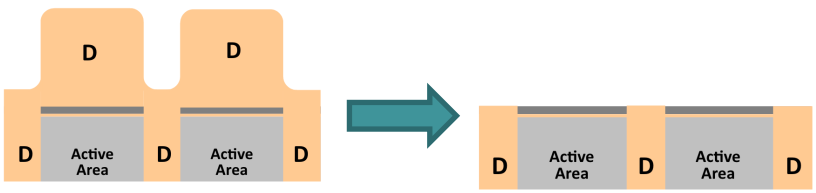
- Due to **high chemical activity of ceria**, ceria slurries have been widely used in the STI CMP Process
- Ceria slurries can be **tailored** to achieve desired **selectivity** between SiO_2 materials and Si_3N_4

Lee, Hyunseop, Hyoungjae Kim, and Haedo Jeong. 2022. "Approaches to Sustainability in Chemical Mechanical Polishing (CMP): A Review." International J ournal of Precision Engineering and Manufacturing-Green Technology 9 (1): 349–67.

Srinivasan, Ramanathan, Pradeep Vr Dandu, and S. V. Babu. 2015. "Shallow Trench Isolation Chemical Mechanical Planarization: A Review." ECS Journal of Solid State Science and Technology 4 (11): P5029–39

I. Introduction and motivation

STI CMP Process



- Due to **high chemical activity of ceria**, ceria slurries have been widely used in the STI CMP Process
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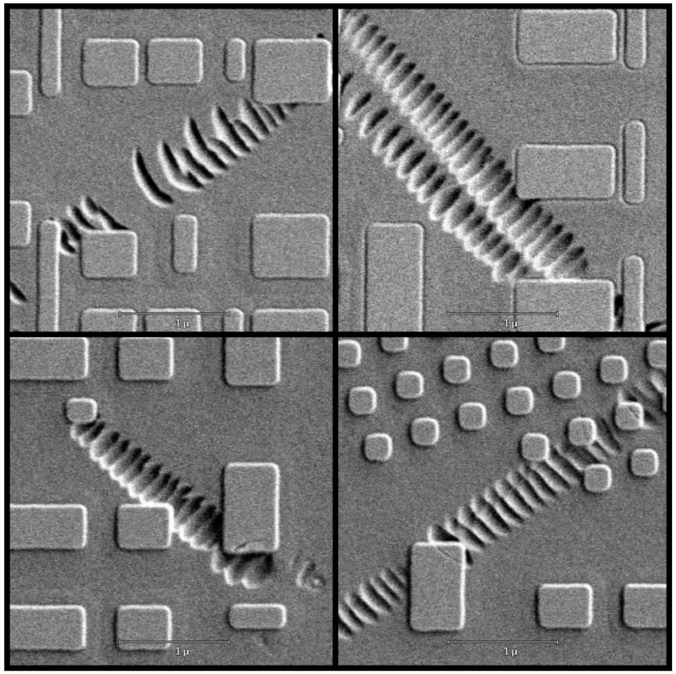
Micro-scratch at post-STI CMP



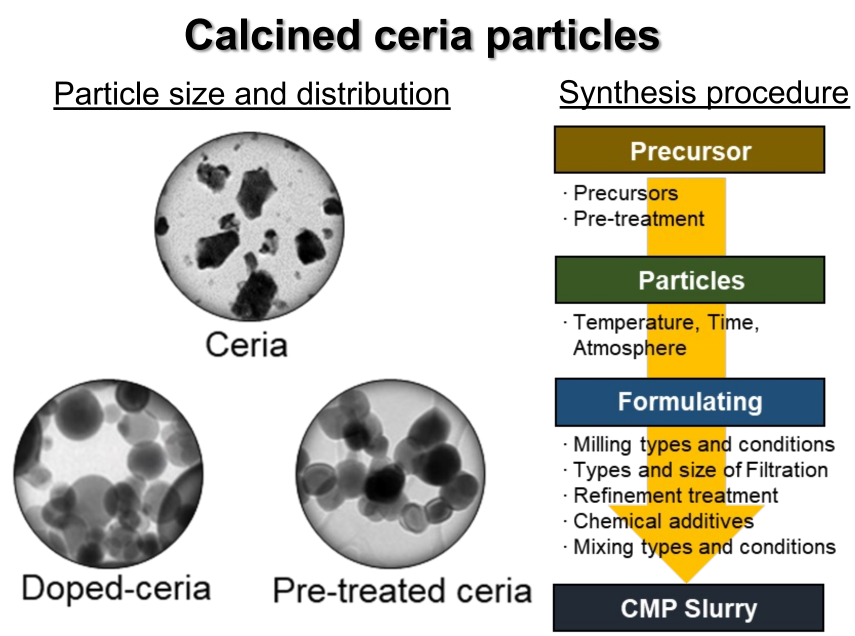
Defect reduction strategies

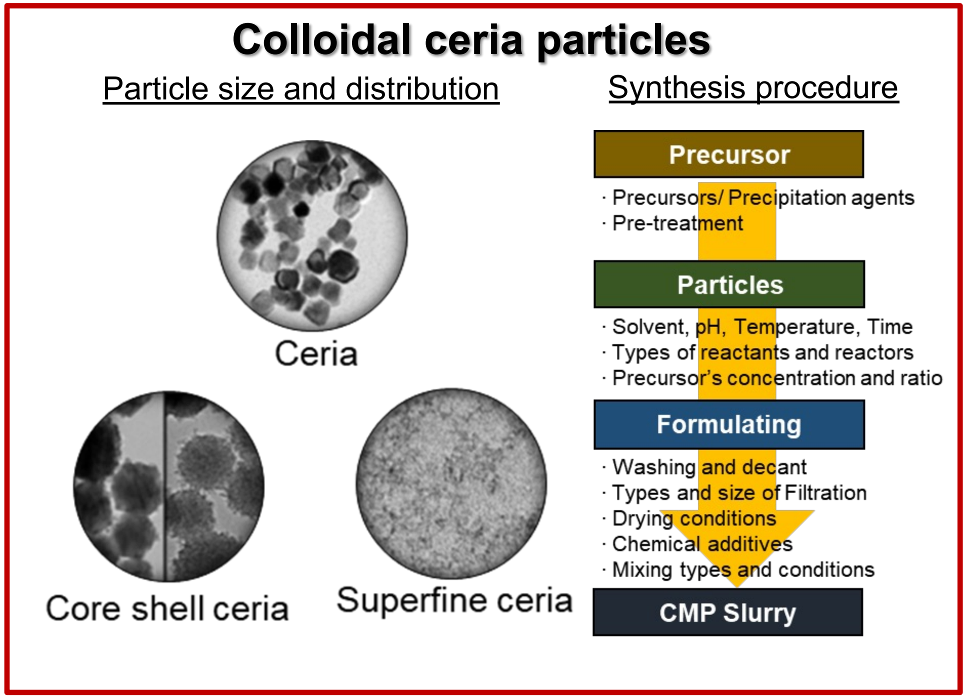
- Tightening particle size distribution, cutting tail, LPC reduction
- Chemistry formulation to prevent particle agglomeration deposition/ re-deposition to wafer surface
- Moving toward chemical polishing rather than mechanical, abrasive content reduction
- Changing to Colloidal particle, Decreasing particles size

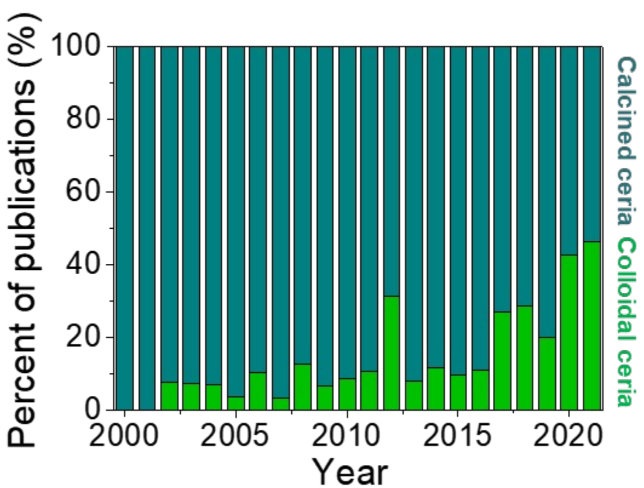
Krishnan, Mahadevaiyer, Jakub W. Nalaskowski, and Lee M. Cook. 2010. "Chemical Mechanical Planarization: Slurry Chemistry, Materials, and Mechanisms." Chemical Reviews 110 (1): 178–204

II. Research objectives

Trends of ceria slurries



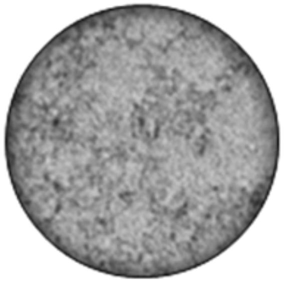




Overall publication trend for calcined and colloidal ceria particles for CMP applications during 2000-2021.

J. Seo, K. Kim, K. Kang, and S.V. Babu, Recent advances and perspectives on ceria particle applications in CMP, *ECS J Solid State Sci.*, 2022, 11, 084003.

Objectives

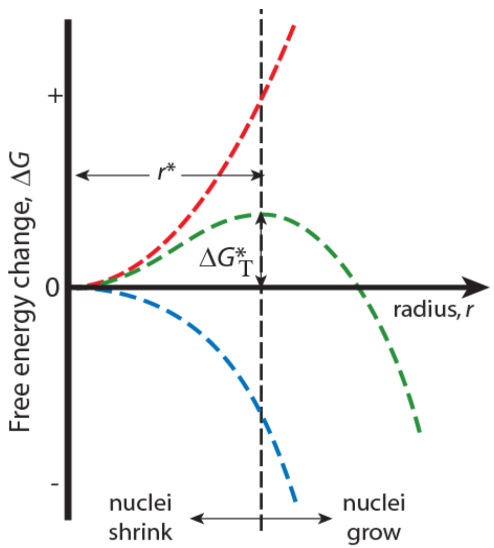

Superfine ceria

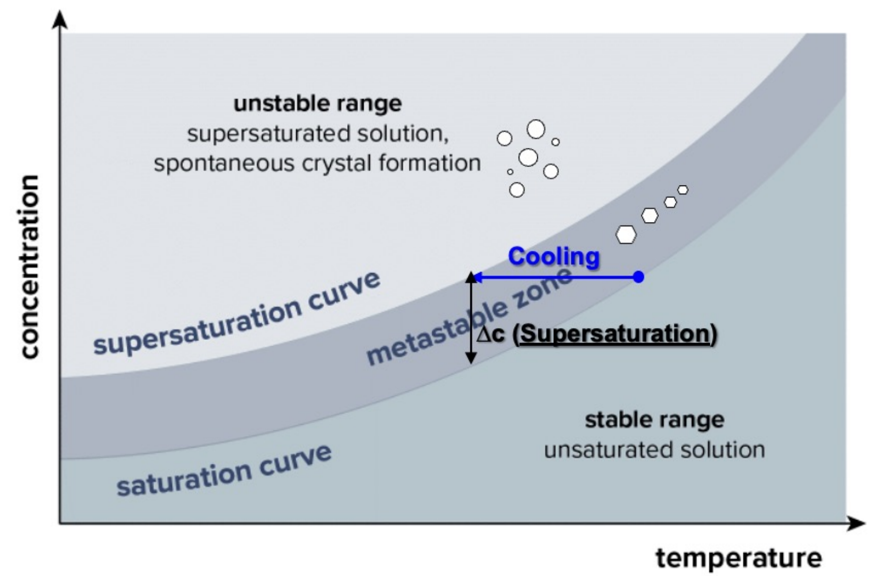
- Addressing the lower removal rates of smaller ceria nanoparticles
- Understanding the removal mechanisms of superfine ceria

III. Experimental materials and Procedure

III. Experimental materials and Procedure

How can we control the nucleation and growth of nano particles in solution?





Critical nucleus:

$$r^* = \frac{2\gamma V_m}{RT \, In S}$$

→ Supersaturation

→ Temperature

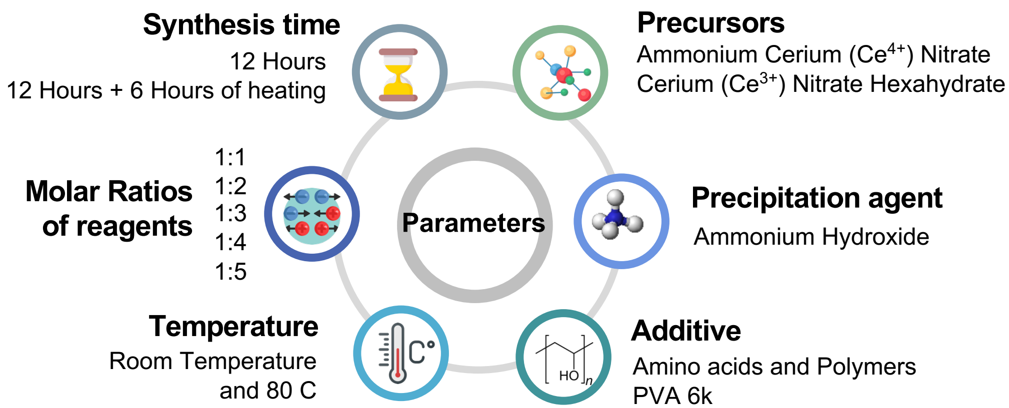
Key synthesis parameters

- **Precursors**
- **Precipitation agent**
- **Additive**
- **Synthesis time**
- **Molar Ratios of reagents**

→ **Supersaturation!**

D.A. Porter, K.E. Easterling, M. Sherif, Phase Transformations in Metals and Alloys, (Revised Reprint), CRC press, 2009.

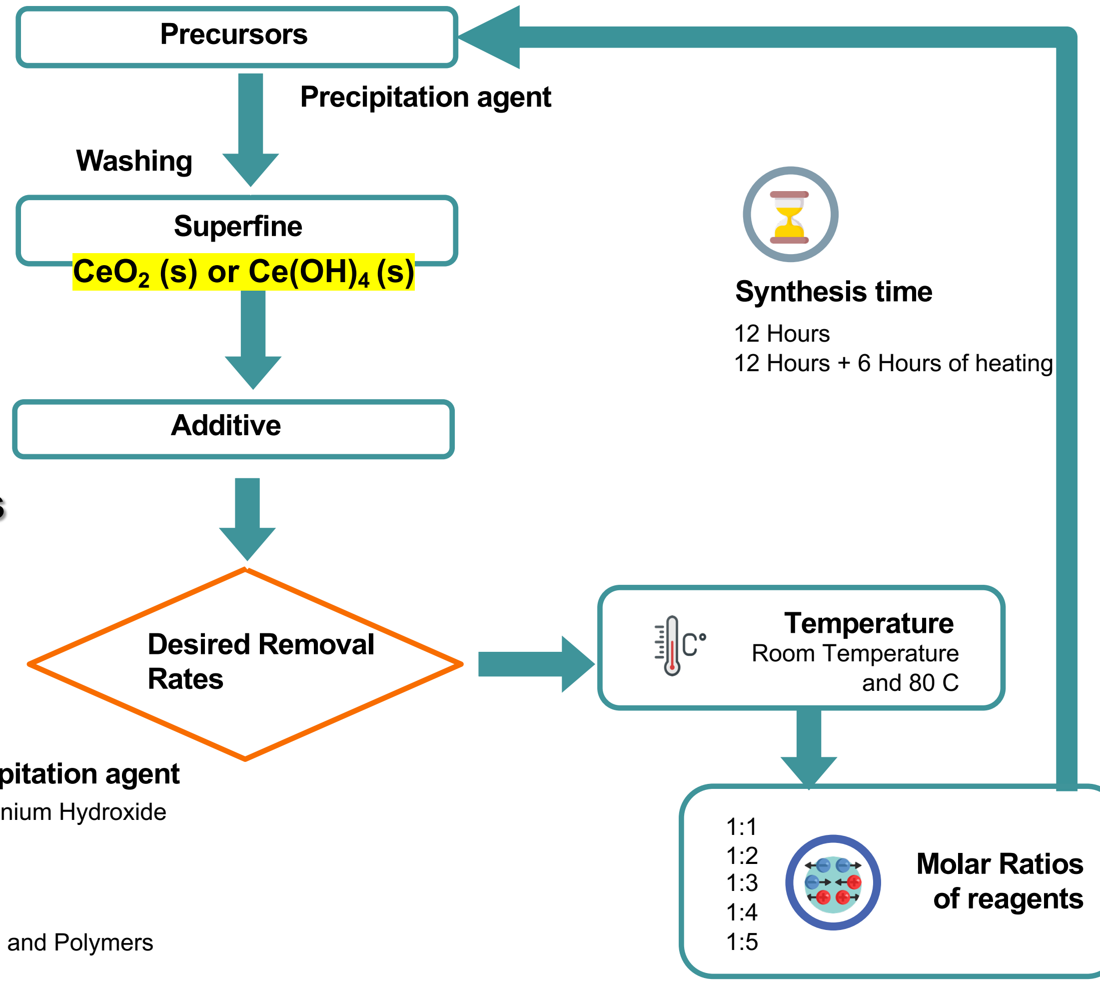
Key synthesis parameters



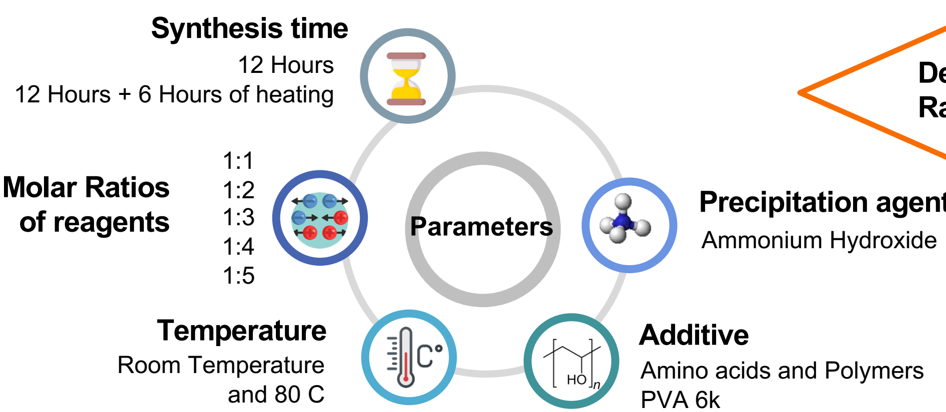
III. Experimental materials and Procedure

Ce(III)/Ce^{3+} :
Cerium(III) Nitrate $Ce(NO_3)_3$ **or**

Ce(VI)/Ce^{4+} :
Ammonium Cerium(IV) Nitrate: $(NH_4)_2 \cdot (Ce(NO_3)_6)$

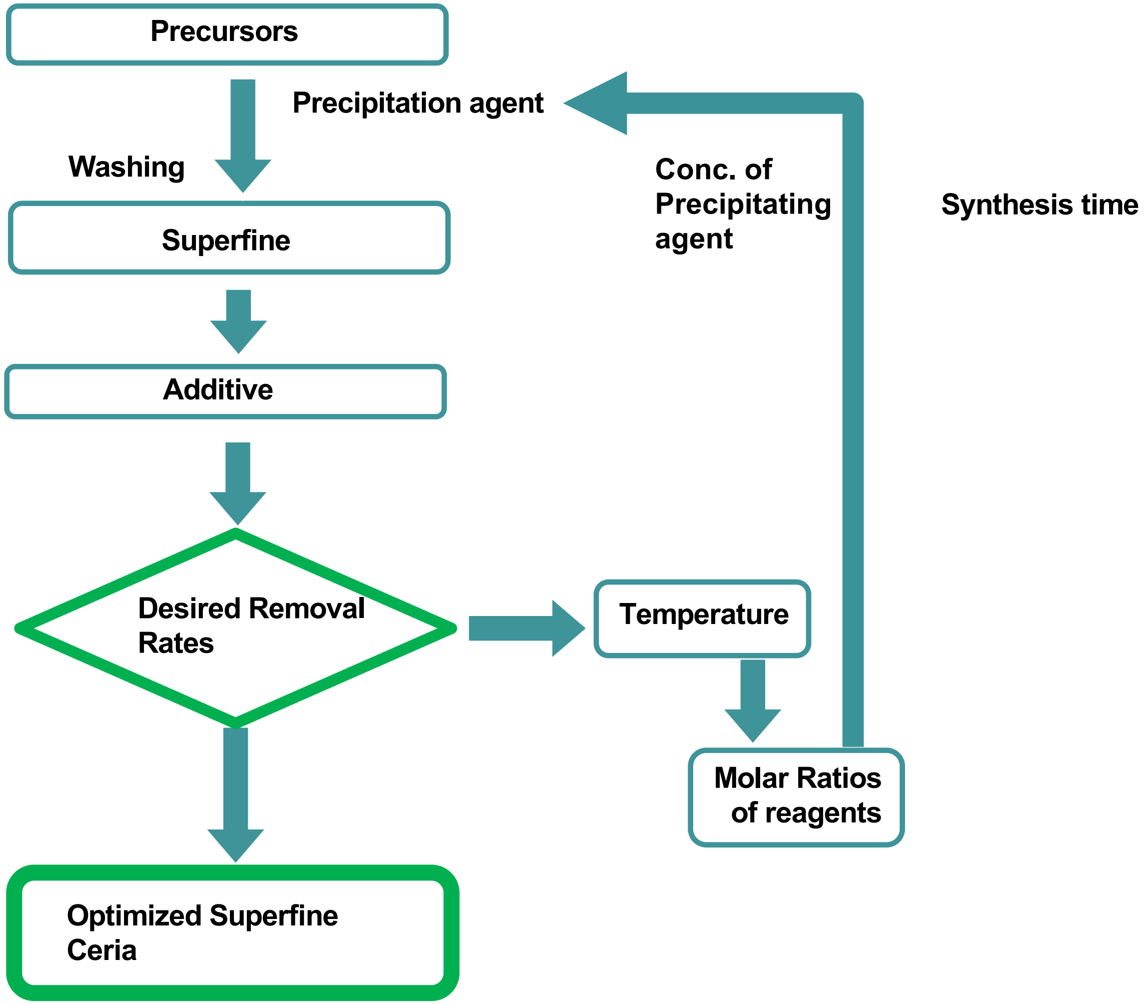


Key synthesis parameters



III. Experimental materials and Procedure

Flowchart of the synthesis process



Sequence of decision process

VI. Results and Discussion

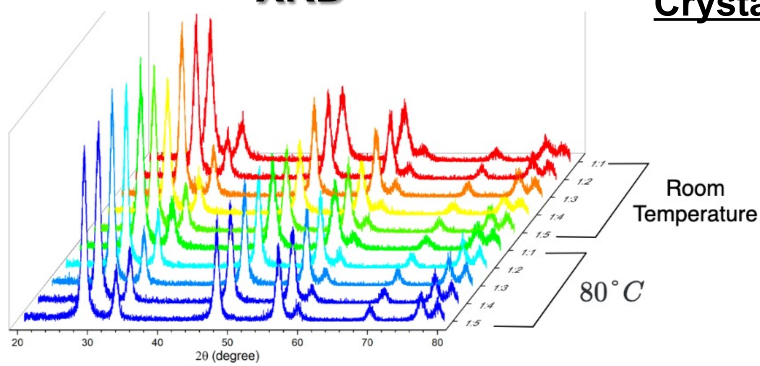
The effect of the precursors on the formation of CeO_2

+Molar ratio of $Ce^{3+\text{ or }4+}/OH^-$ + Temperature

Cerium(Ⅲ) Nitrate Hexahydrate: $Ce(NO_3)_3 \cdot 6H_2O$

$2Ce(NO_3)_2$ (aq) + $6NH_4OH$ (aq) → $2Ce(OH)_3$ (s) + $6NH_4NHO_3$ (aq) + $1/2O_2$ → **$2CeO_2$ (s)** + $3H_2O$ + $6NH_4NO_3$ (aq)

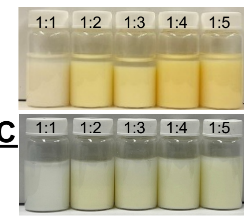
XRD

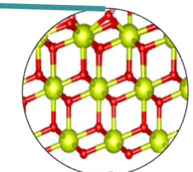


Crystallization!

at RT

at 80 °C





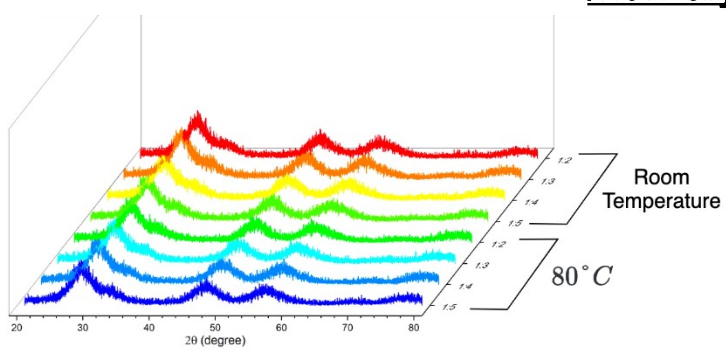
Ce(III)

High crystalline particle

Ammonium Cerium(IV) Nitrate: $(NH_4)_2 \cdot (Ce(NO_3)_6)$

$(NH_4)_2 \cdot Ce(NO_3)_6$ (aq) + $4NH_4OH$ (aq) → **$Ce(OH)_4$ (s) or $CeO_2 \cdot 2H_2O$** + $6NH_4NO_3$ (aq)

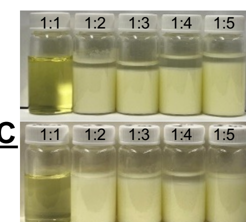
XRD



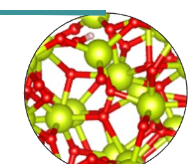
Precipitation!
/Low crystallinity

at RT

at 80 °C



No Nucleation



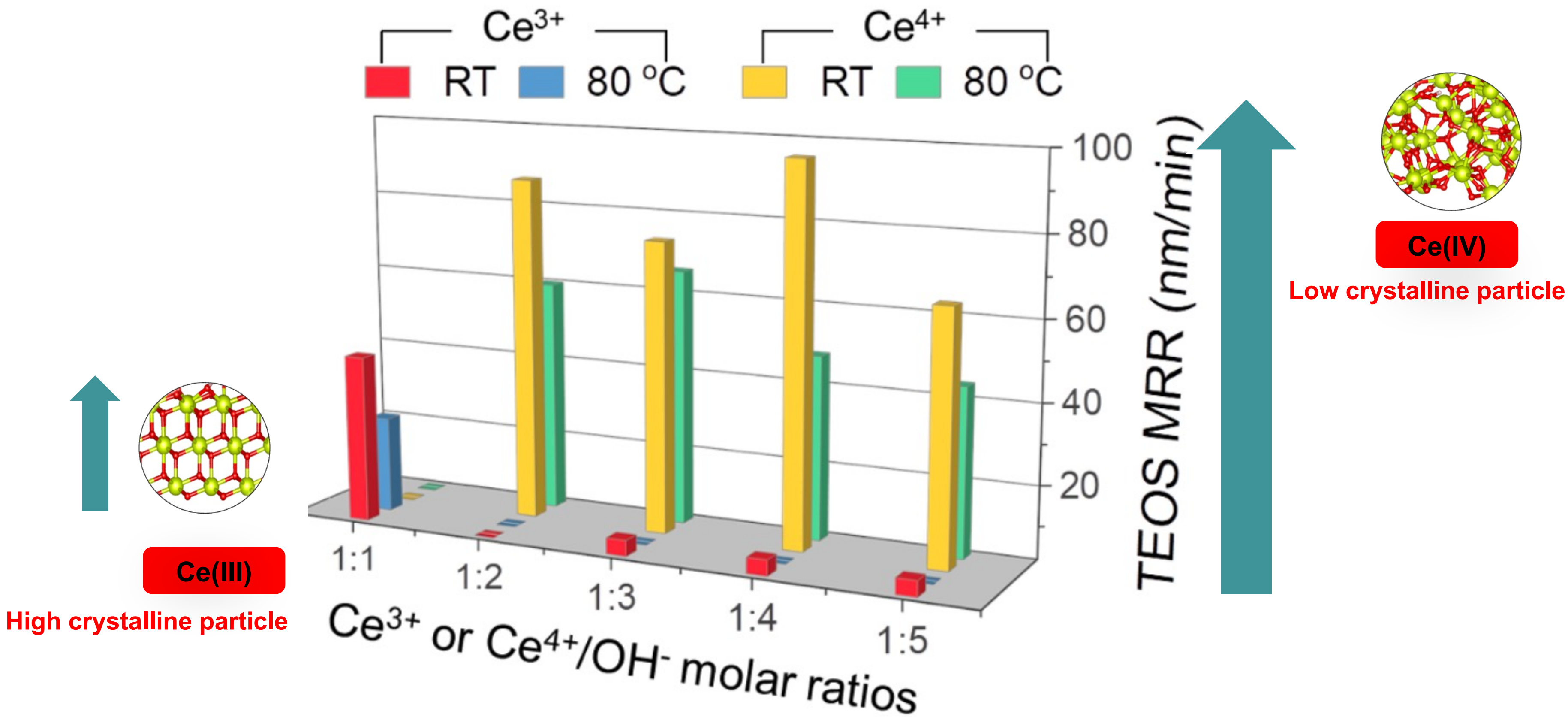
Ce(IV)

Low crystalline particle

Significant changes in TEOS removal rates due to key synthesis parameters

Cerium(Ⅲ) Nitrate Hexahydrate: $Ce(NO_3)_3 \cdot 6H_2O$

Ammonium Cerium(IV) Nitrate: $(NH_4)_2 \cdot (Ce(NO_3)_6)$



- We have observed large differences in removal rates between superfine ceria samples synthesized with differ ent precursors $Ce(NO_3)_3 \cdot 6H_2O$ and $(NH_4)_2 \cdot (Ce(NO_3)_6$ under the same conditions

Why?

Our focus: Mechanisms of SiO_2 CMP using ceria-based slurries

Physical properties (Mechanical action)

· Particle shape, size, and distribution

· Crystallinity

Chemical properties (Chemical action)

· Surface species/defects (e.g., OH, Ov, Ce^{3+}, NO_3, etc.)

· Types of Ce-O-Si chemical bond

· Electrostatic Interaction

Slurry properties

· Dispersant stability

· pH adjusting agent, Chemical additives for high polish rates and removal selectivity

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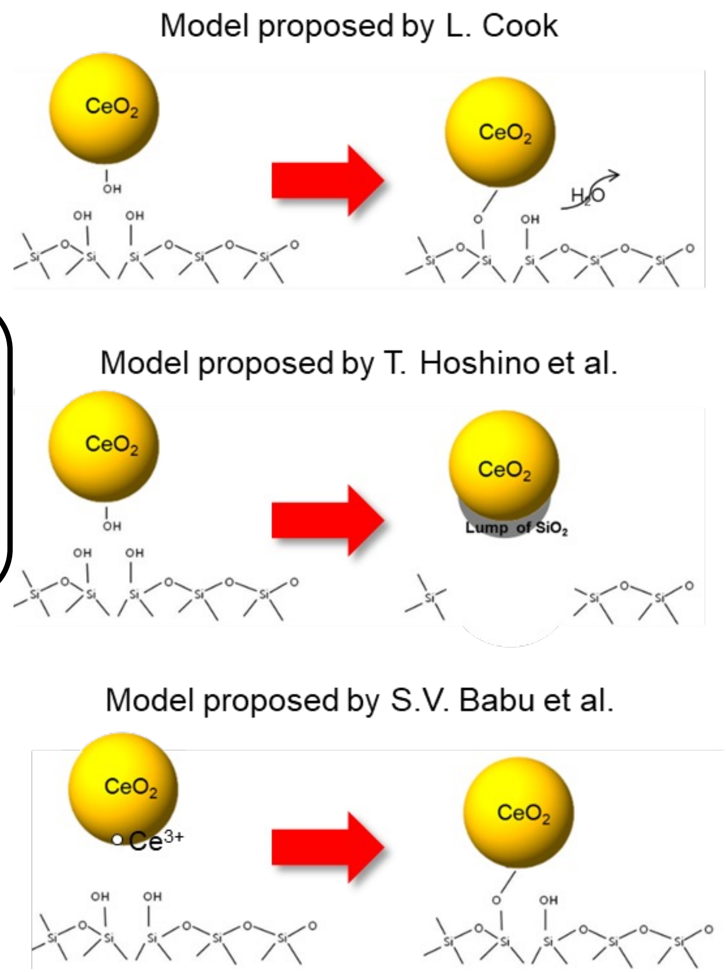
Our focus!

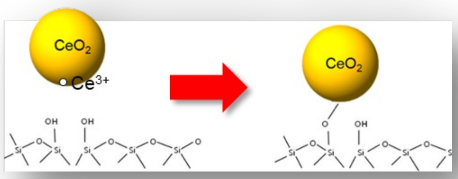


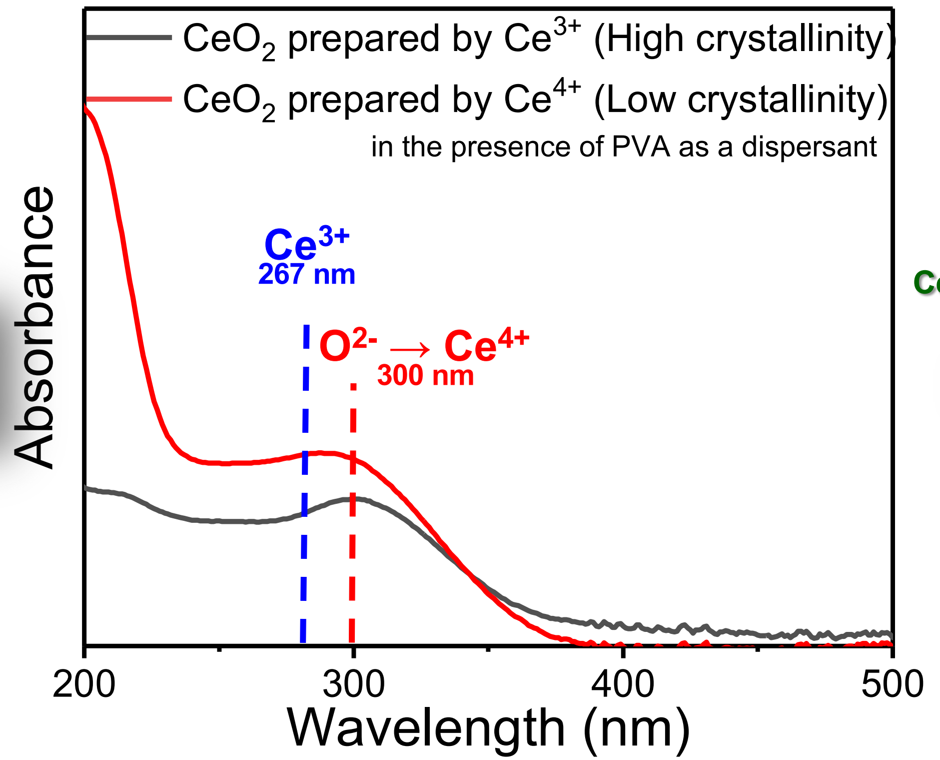
J. Seo. A review on chemical and mechanical phenomena at the wafer interface during chemical mechanical planarization. *Journal of Materials Research* 36 (2021): 235-257.

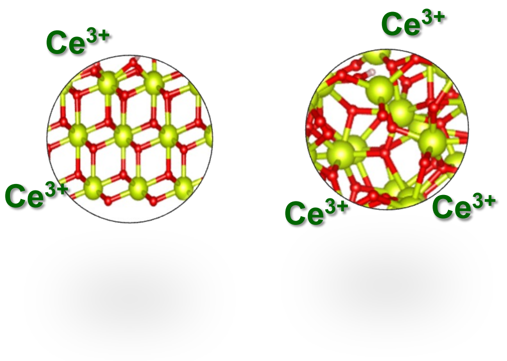
Chemical properties:
Surface species/defects (e.g., Ce^{3+}, OH, Ov, NO_3, etc.)

UV-vis spectroscopy of Superfine CeO_2 particles prepared by Ce^{3+} and Ce^{4+}

Model proposed by S.V. Babu et al.



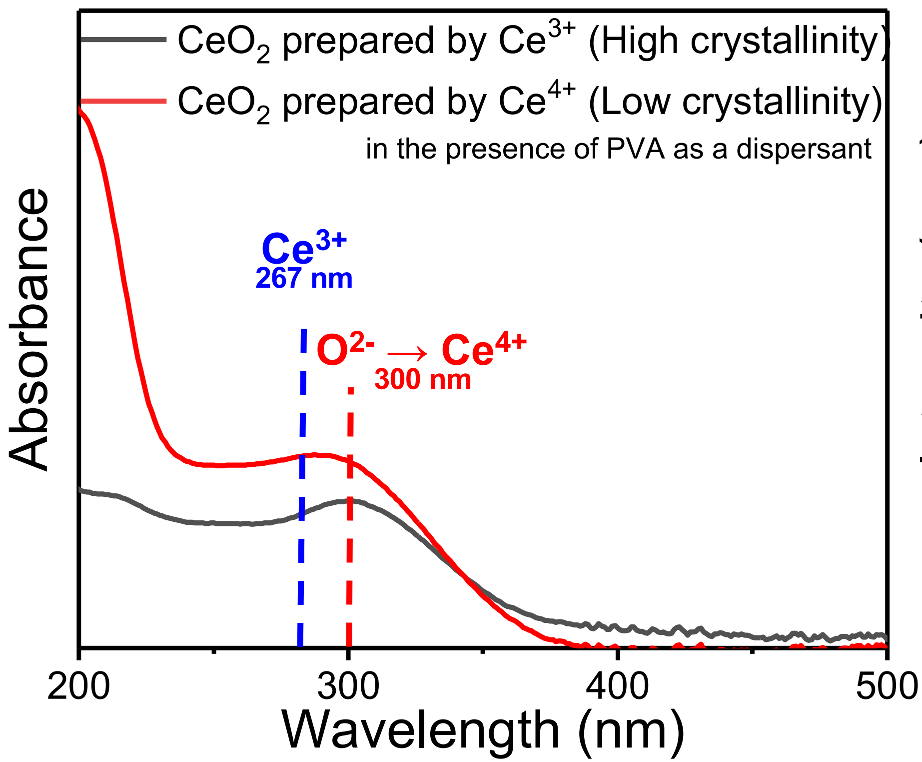




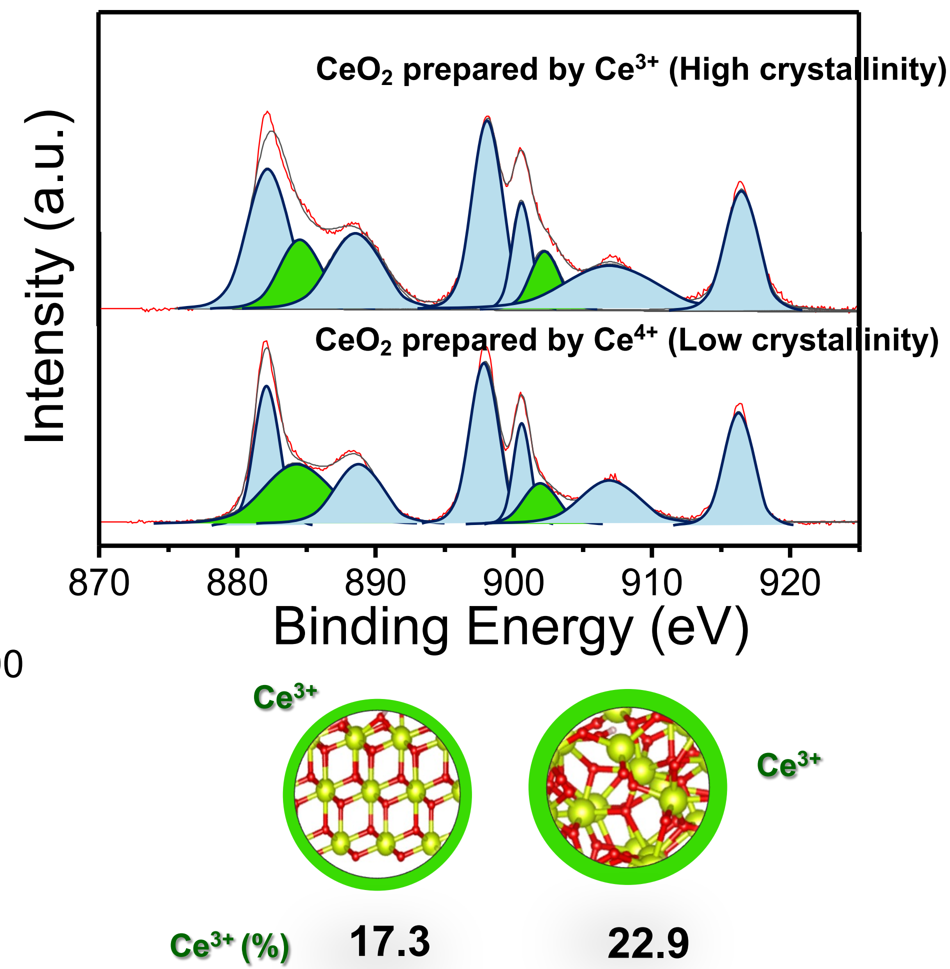
- Ceria prepared using Ce^{4+} has more Ce^{3+} on its surface, as shown by the peak shift in its UV/vis spectra.

Chemical properties:
Surface species/defects (e.g., Ce^{3+}, OH, Ov, NO_3, etc.)

UV-vis spectroscopy of Superfine CeO_2 particles prepared by Ce^{3+} and Ce^{4+}



Ce3d XPS spectra of CeO_2 particles



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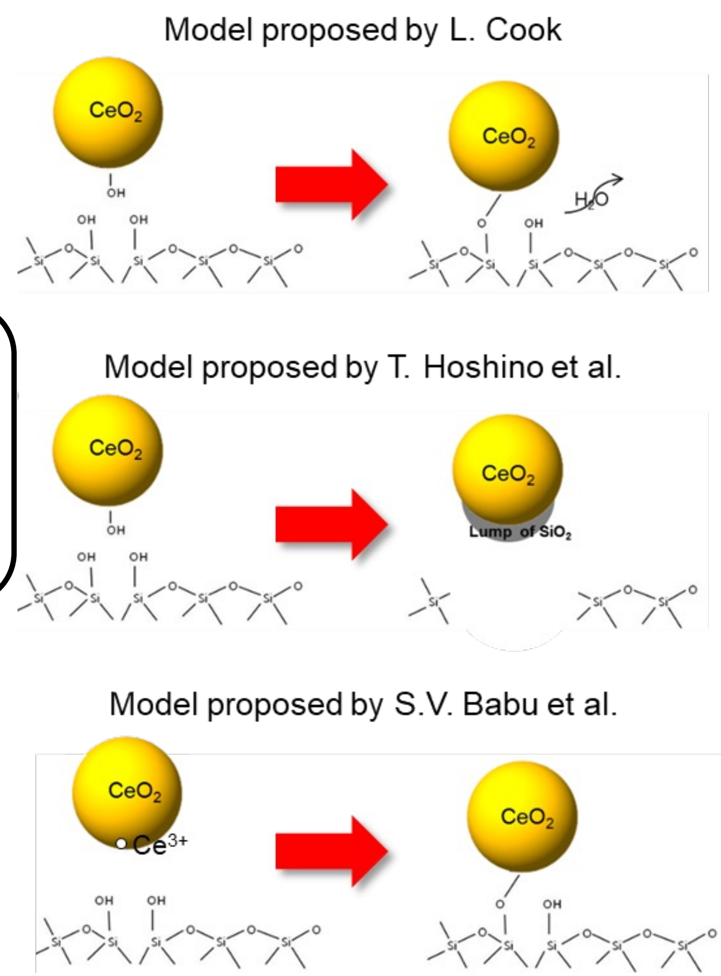
Chemical properties (Chemical action)

· Surface species/defects (e.g., OH, Ov, Ce^{3+}, NO_3, etc.)

· Types of Ce-O-Si chemical bond

· Electrostatic Interaction

Our focus!



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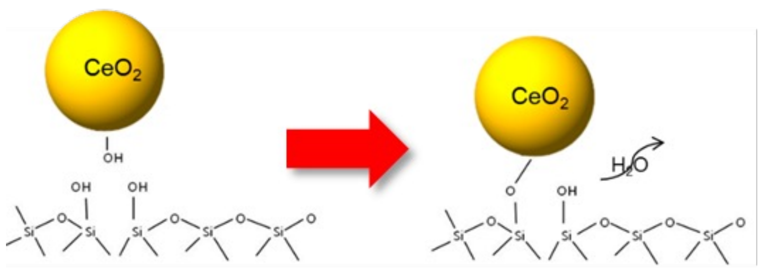
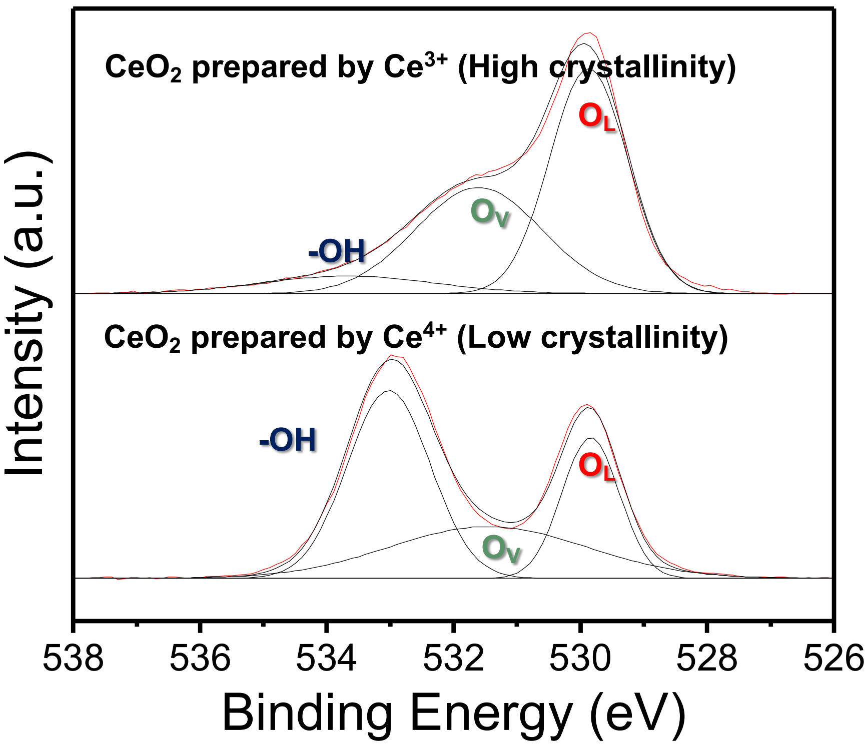
Chemical properties:
Surface species/defects (e.g., OH, Ov, Ce^{3+}, NO_3, etc.)

Model proposed by L. Cook



O1s XPS spectra of CeO_2 particles prepared by Ce^{3+} and Ce^{4+}



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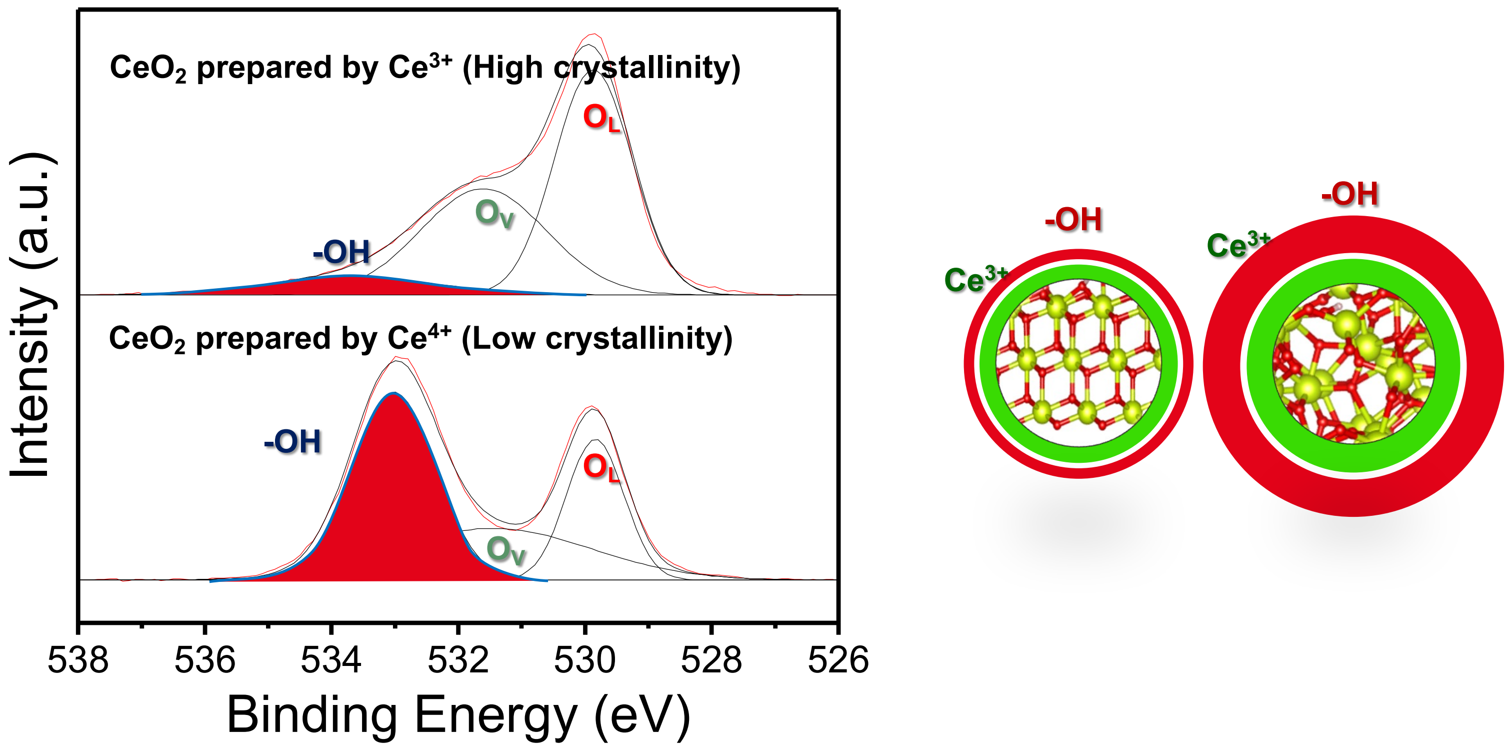
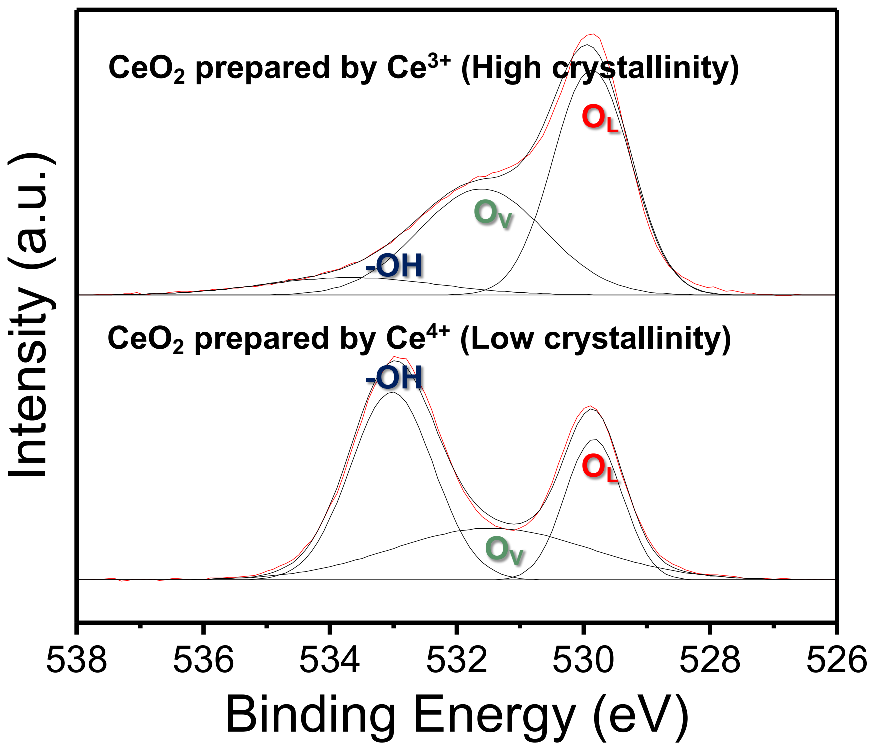


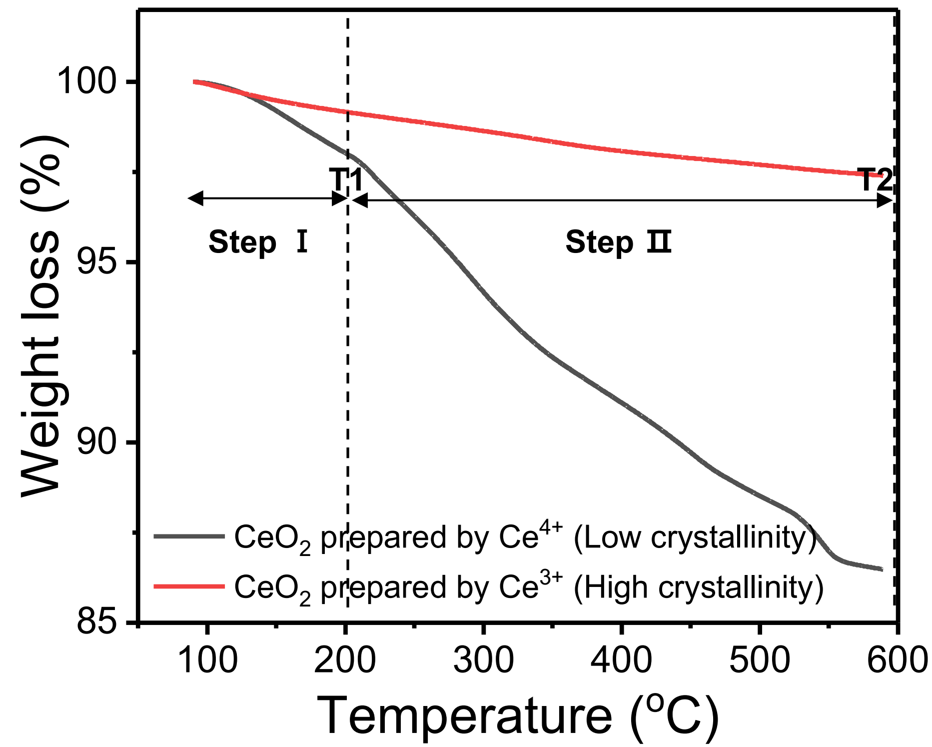
- Ceria prepared using Ce^{4+} Precursor has more OH groups on its surface than that prepared using Ce^{3+} Precursor
- The reason for the higher concentration of −OH groups in superfine ceria prepared using Ce^{4+} is because they are the dominant surface species, which is consistent with the O1s XPS peak.

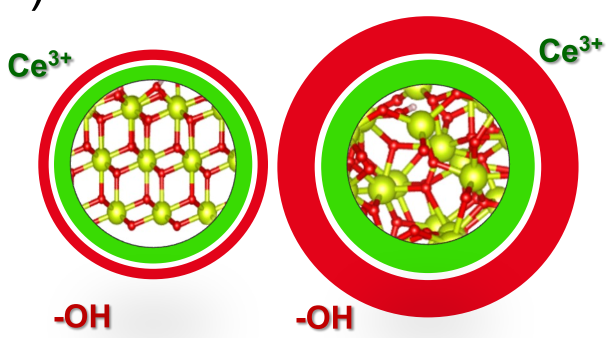
Chemical properties:
Surface species/defects (e.g., OH, Ov, Ce^{3+}, NO_3, etc.)

O1s XPS spectra of CeO_2 particles prepared by Ce^{3+} and Ce^{4+}



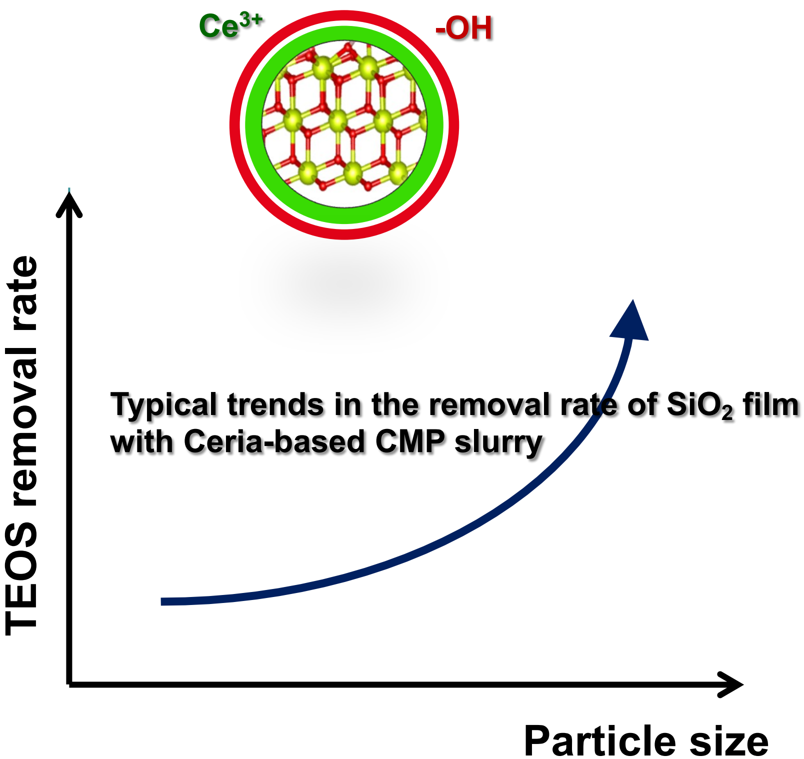
TGA graphs of CeO_2 particles prepared by Ce^{3+} and Ce^{4+}



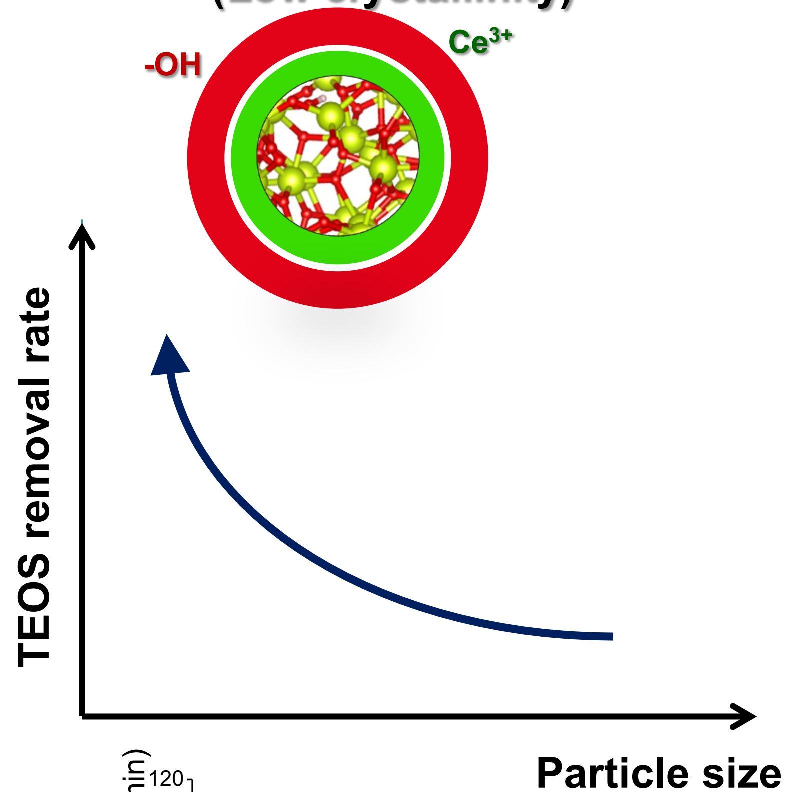


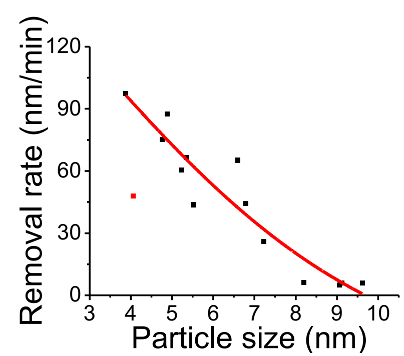
Chemical properties:
Surface species/defects (e.g., OH, Ov, Ce^{3+}, NO_3, etc.)

Superfine CeO_2 particles prepared by Ce^{3+} (High crystallinity)

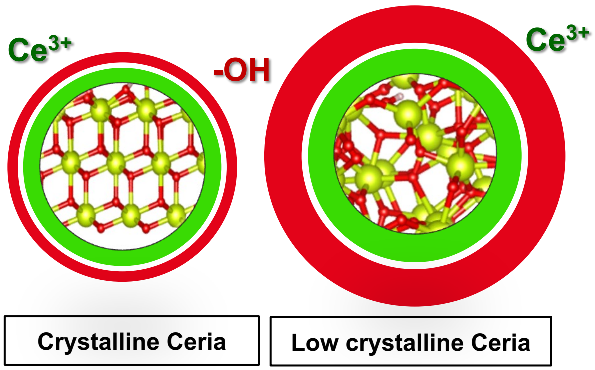


Superfine CeO_2 particles prepared by Ce^{4+} (Low crystallinity)



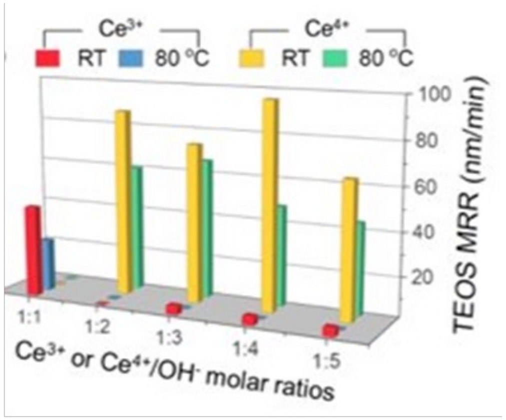


Chemical properties: Understanding types of Ce-O-Si chemical bonds through DFT

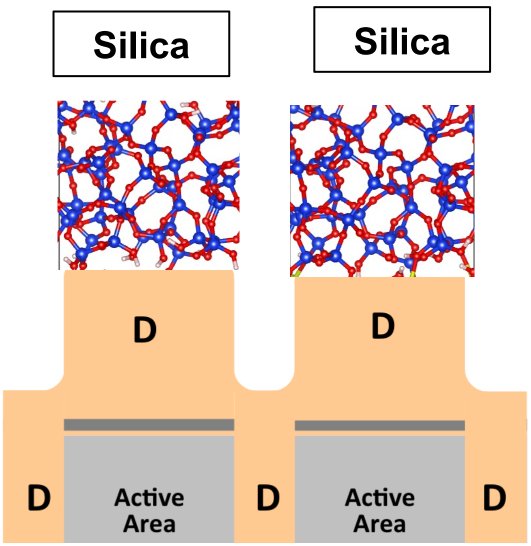


Structural differences significantly influence the TEOS removal rate

What causes the higher RR?



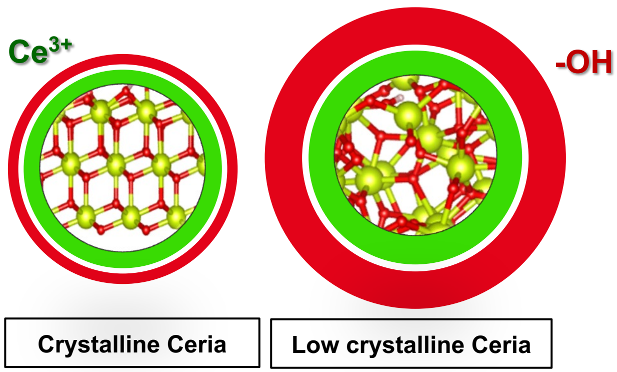
Interfacial strength between silica/ceria ?



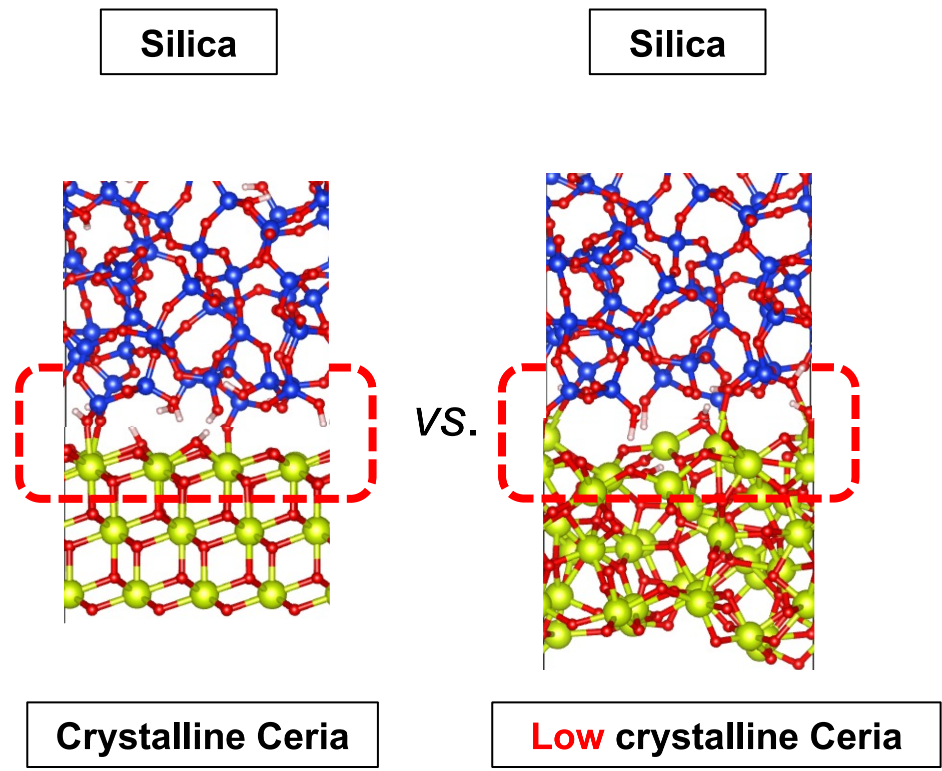
✓ ***Interfacial strength***

- During CMP process, the interface of silica/ceria will be formed.
- Stronger interfacial strength may increase the removal rate of silica.
- *Does amorphous ceria have a stronger adhesion with the silica surface?*

Chemical properties: Understanding types of Ce-O-Si chemical bonds through DFT

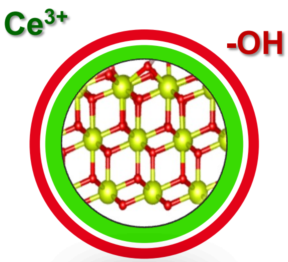


✓ ***Interfacial strength***



Chemical properties: Understanding types of Ce-O-Si chemical bonds through DFT

✓ ***Interfacial strength crystalline ceria and different surface chemistries***

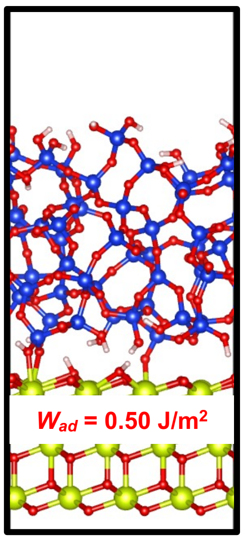


Crystalline Ceria

Chemical properties: Understanding types of Ce-O-Si chemical bonds through DFT (crystalline ceria/silica)

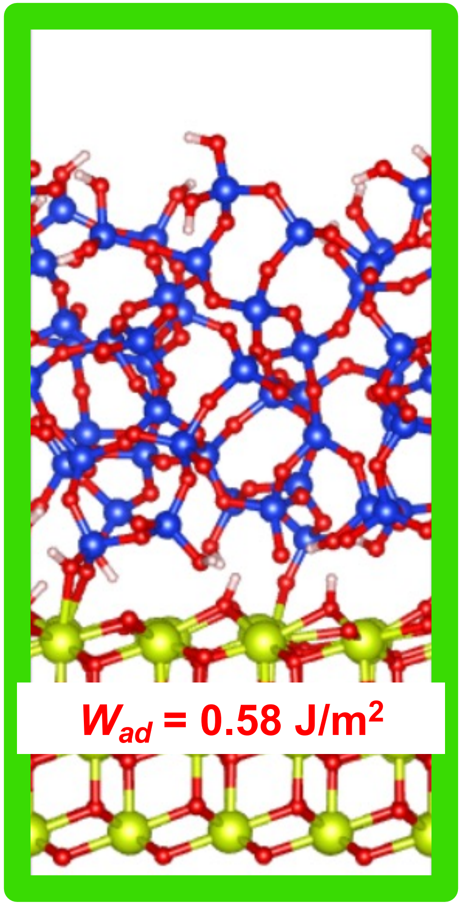
1. Work of adhesion (W_{ad}) of c-ceria/silica with different surface chemistries

silica/*c*-ceria



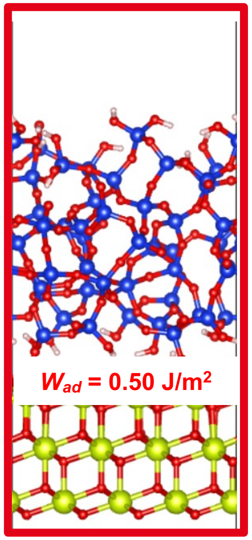
silica/*c*-ceria

with Ce^{3+}



silica/*c*-ceria

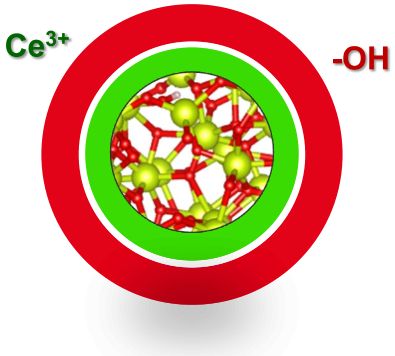
with OH



· The value of W_{ad} for silica/*c*-ceria is 0.50 J/m^2, and that for *c*-ceria/silica with **Ce^{3+} species** and OH groups is 0.58 and 0.50 J/m^2, respectively

Chemical properties: Understanding types of Ce-O-Si chemical bonds through DFT

✓ ***Interfacial strength low crystalline ceria and different surface chemistries***

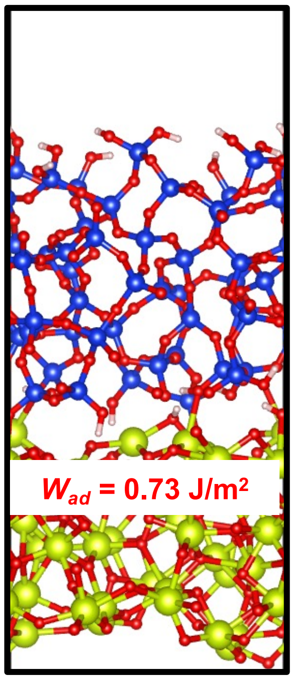


Low crystalline Ceria

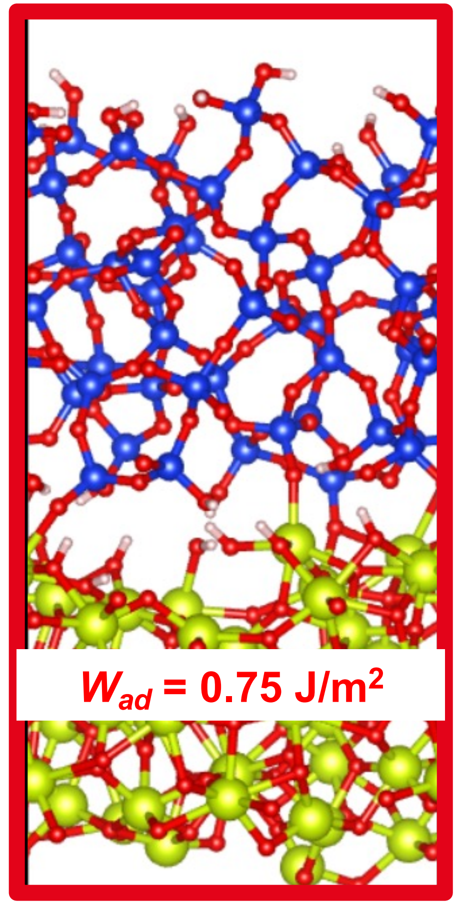
Chemical properties: Understanding types of Ce-O-Si chemical bonds through DFT (amorphous ceria/silica)

2. Work of adhesion (W_{ad}) of *α*-ceria/silica with different surface chemistries

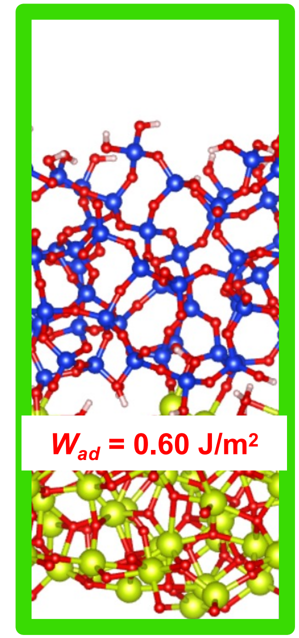
silica/*α*-ceria



silica/*α*-ceria
with OH



silica/*α*-ceria
with Ce^{3+}



· The value of W_{ad} for silica/*α*-ceria is 0.73 J/m², and that for *α*-ceria/silica with O vacancies and OH groups is 0.60 and 0.75 J/m², respectively.

Summary

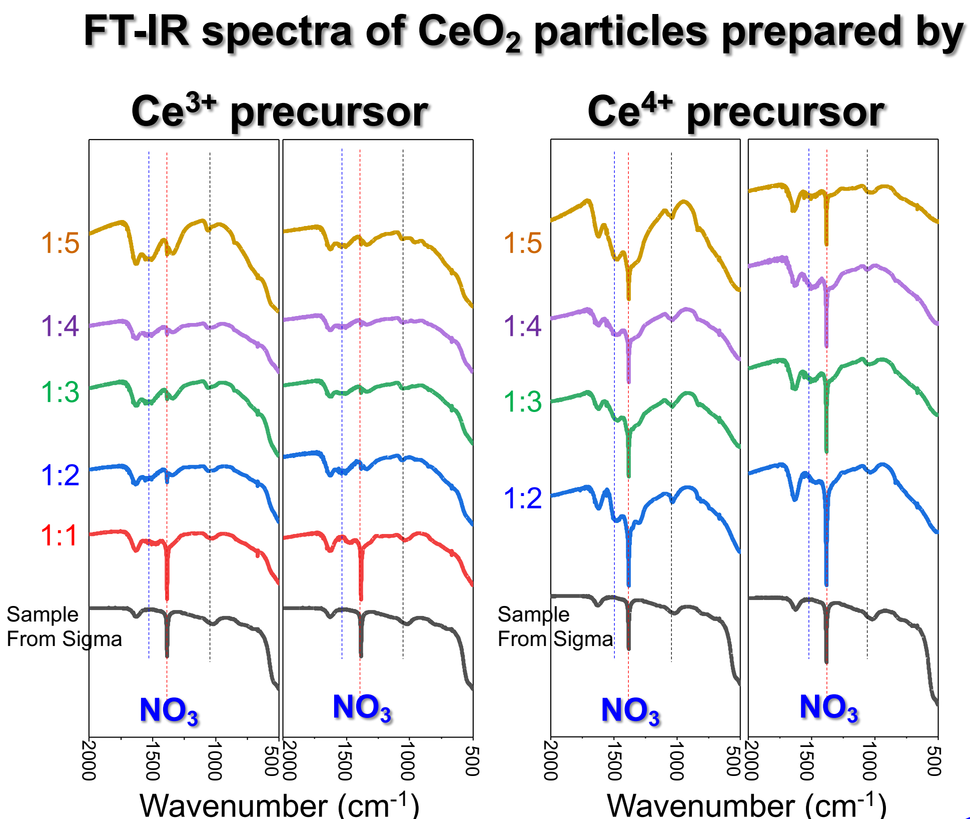
- **Superfine ceria particles** prepared using **Ce(IV) have more Ce^{3+} on their surface**, as shown by their UV/vis spectra and XPS.

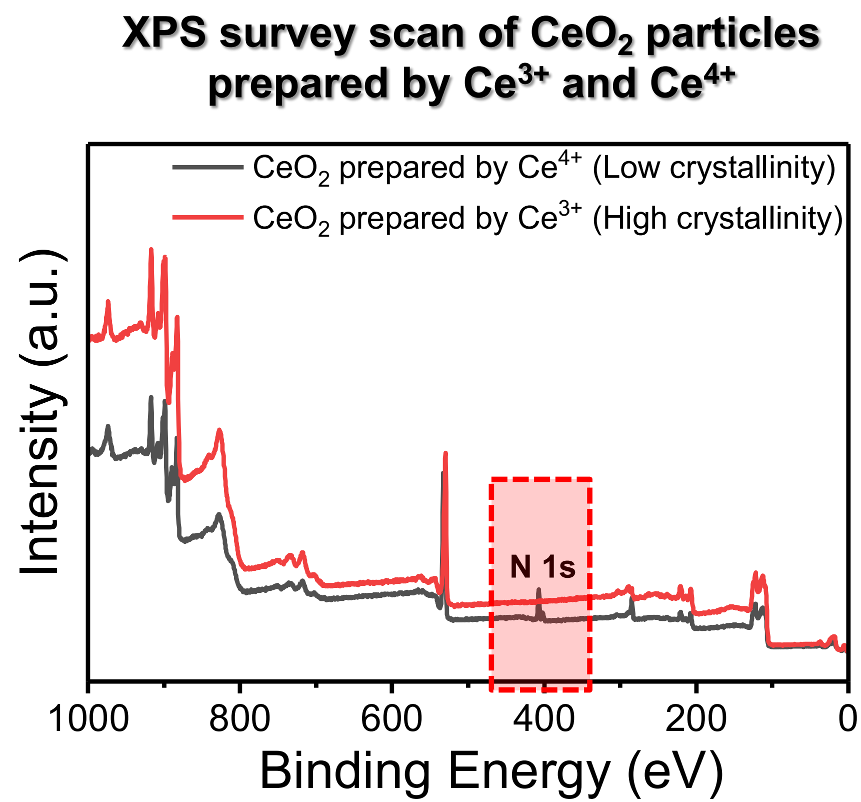
- Superfine ceria prepared using **Ce(IV) (low crystallinity) has a higher concentration of -OH groups** on its surface, making them the dominant surface species. The reason for the higher concentration of -OH groups in superfine ceria prepared using Ce(IV) are the **dominant species**, may be due to the. **disordered** surface structure

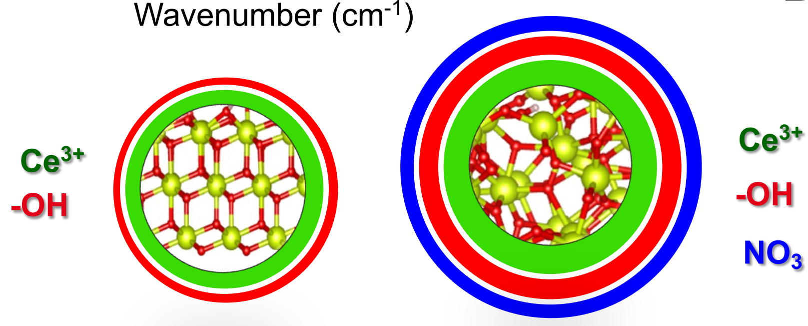
- We studied the **polishing mechanisms** of superfine ceria particles through **DFT calculation** and found that **low crystalline superfine ceria removed SiO_2 through condensation**, while Ce^{3+} was the active site for polishing with crystalline ceria (a generally acceptable polishing mechanism). **Low crystalline ceria surfaces have higher adhesion energies** and could enhance the removal rate of SiO2 film during polishing

Future work

- **Investigating effect of Nitrate groups present on surface of ceria particles**







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Jihoon Seo, Ph.D.
Assistant Professor
Department of Chemical & Biomolecular Eng, Clarkson University, USA.

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Email: Jseo@clarkson.edu (Assistant Professor, Clarkson University)
Google scholar: https://scholar.google.com/citations?user=bkS82b0AAAAJ&hl=us&authuser=1&oi=sra
Website: https://sites.clarkson.edu/jseo/

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