SFB 986 M³

C6

Synthesis and Thermal Stability of Monodisperse ZrO_2@SiO_2 Core-Shell Submicron Particles

26/06/2017 – Ceramics and Composite Materials, Madrid - Maik Finsel

TUHH
Technische Universität Hamburg-Harburg

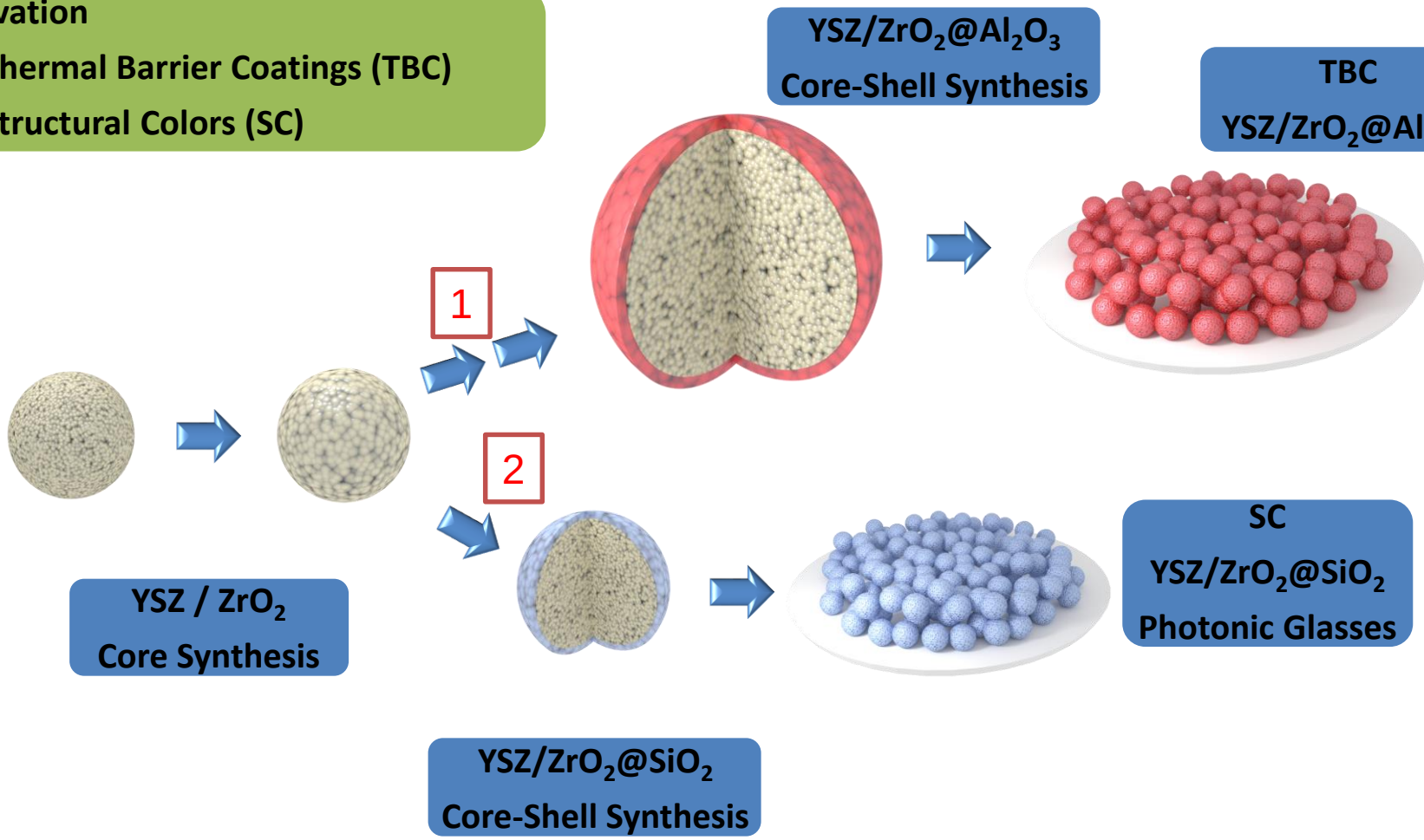
Helmholtz-Zentrum Geesthacht
Zentrum für Material- und Küstenforschung

Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

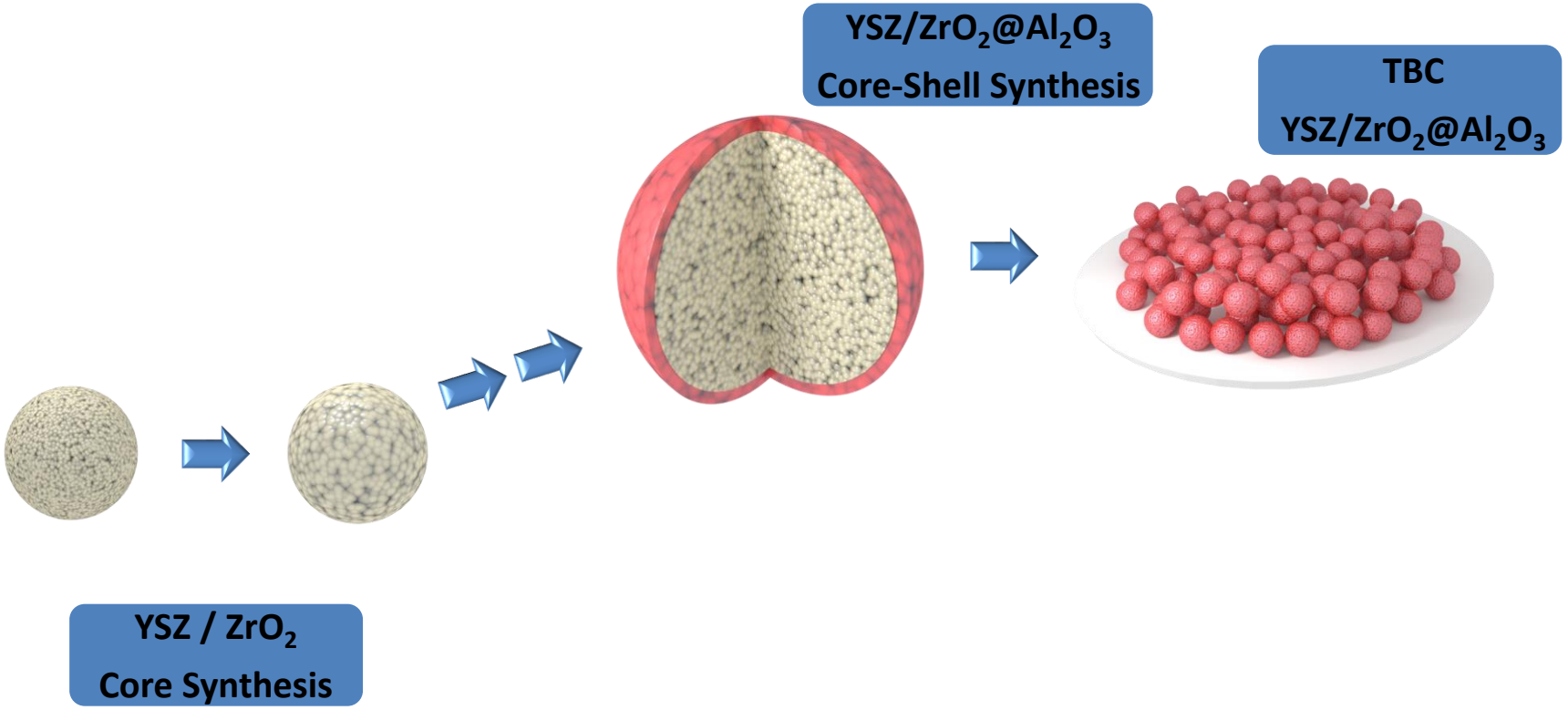
Outline

Motivation

1. **Thermal Barrier Coatings (TBC)**
2. **Structural Colors (SC)**



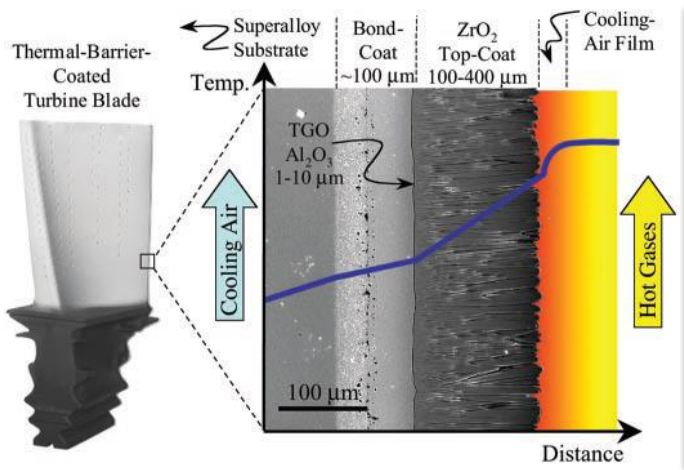
Outline: Thermal Barrier Coatings (TBC)



Y-Stabilized ZrO_2 Microparticles Show High IR-Reflectivity

Motivation: Thermal Barrier Coatings (TBC)

Padture, Gell, Jordan, *Materials Science*, 2002.





photonic TBCs from ceramic microparticles

What is used:

- Yttria-stabilized zirconia bulk (YSZ)
  - ceramic layers
  - electron beam or plasma spray
  - 100 – 300 °C decrease in temperature

What we have:

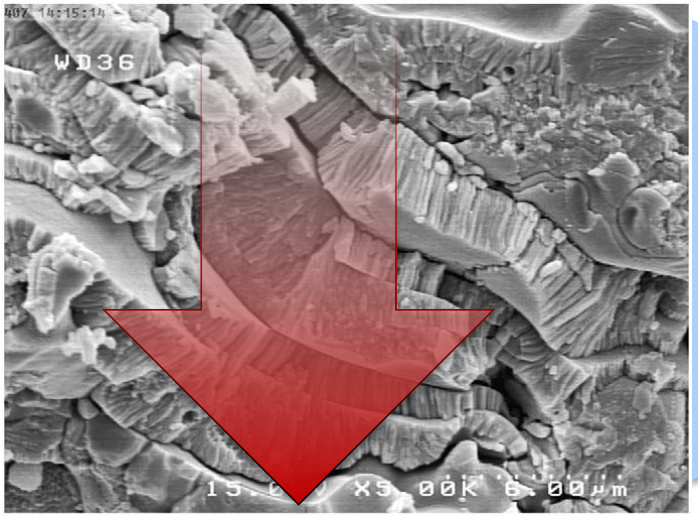
- YSZ microparticles
  - thin layers
  - light weight
  - low heat conduction
  - **high reflectivity in infrared**



Y-Stabilized ZrO_2 Microparticles Show High IR-Reflectivity

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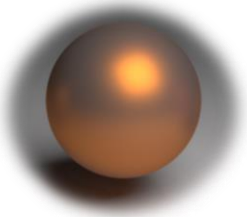
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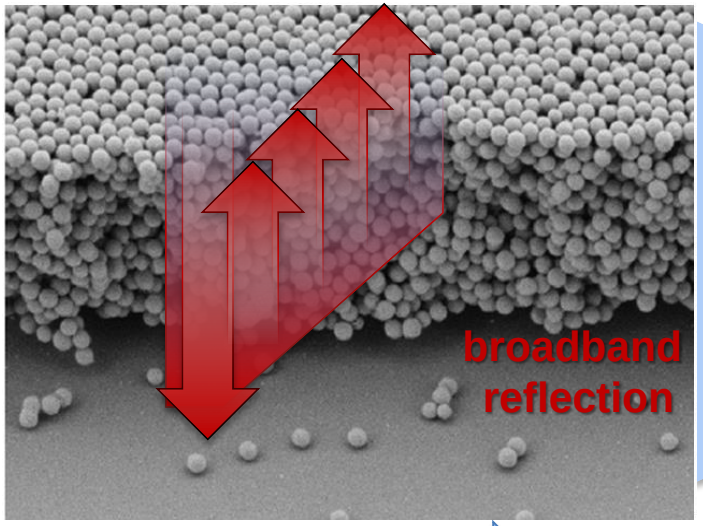
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Y-Stabilized ZrO_2 Microparticles Show High IR-Reflectivity

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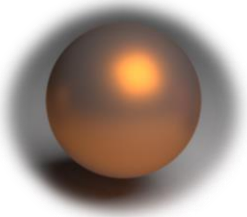
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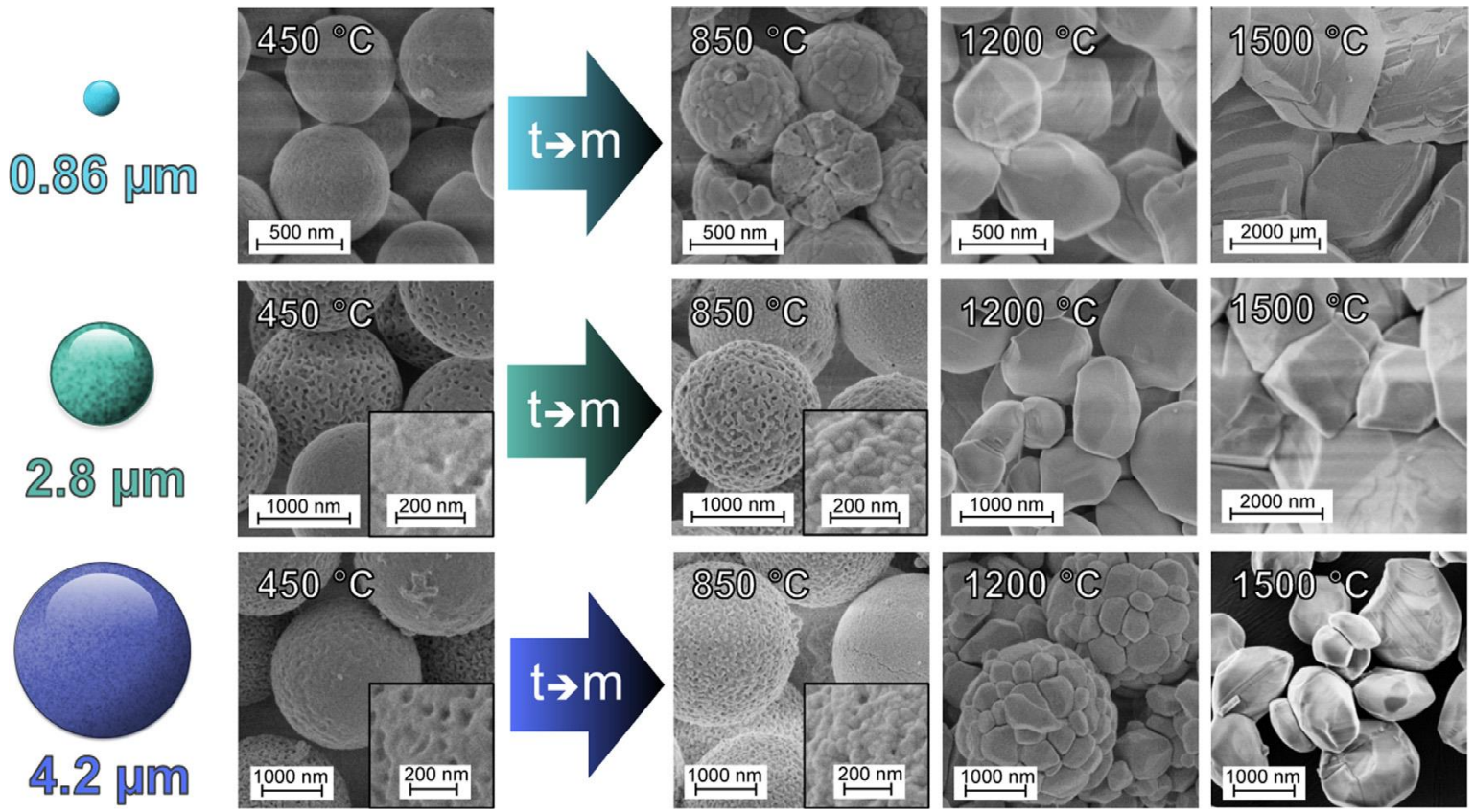
What we have:

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  - light weight
  - low heat conduction
  - **high reflectivity in infrared**



Temperature Stability of ZrO_2 Microparticles is Size Dependent

Temperature Stability of ZrO_2 Investigated by Scanning Electron Microscopy

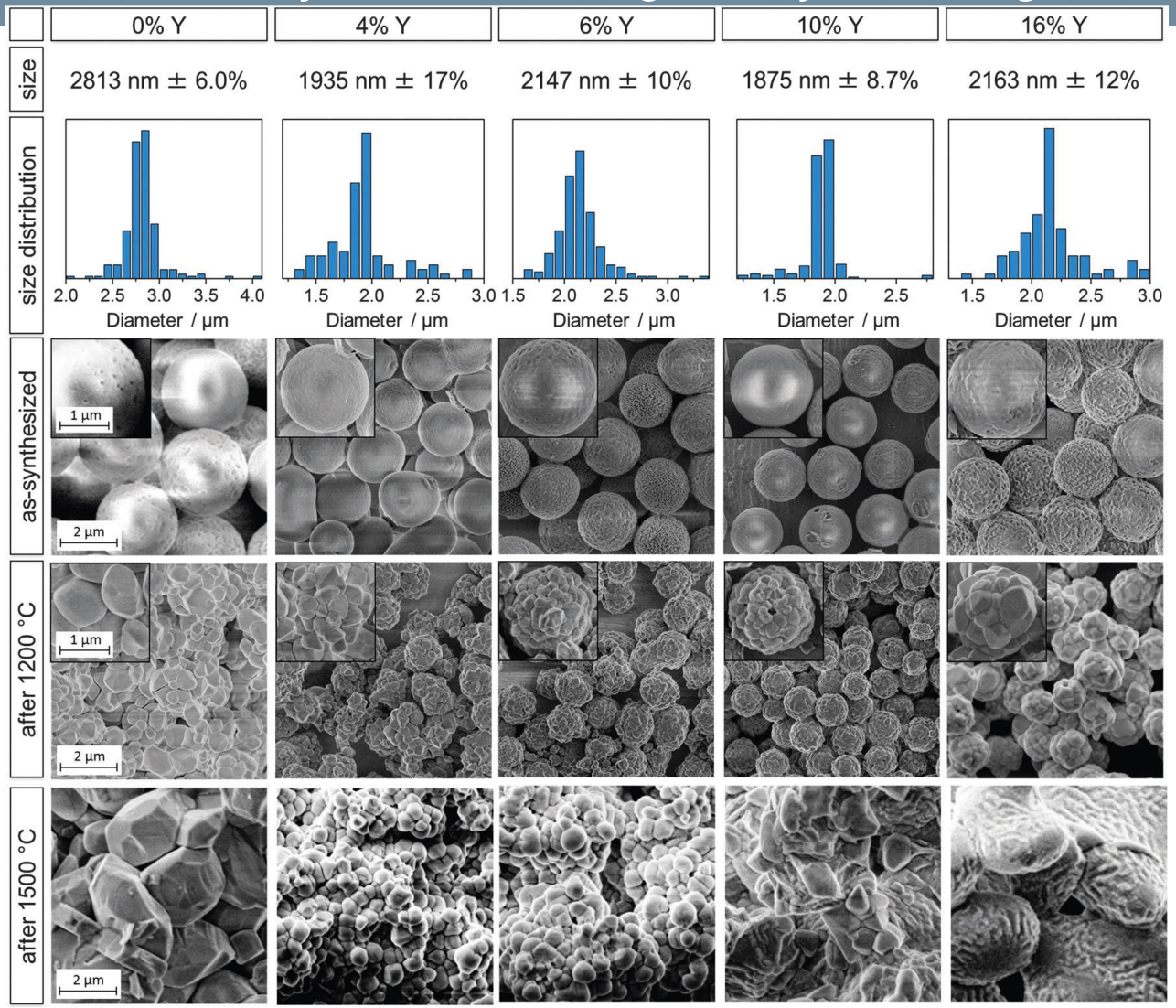


t: tetragonal
m: monoclinic

E. W. Leib *et al., J. Colloid Interface Sci.*, 448, 582-592, **2015**.

Improved Temperature Stability of Y-Stabilized ZrO_2 Microparticles

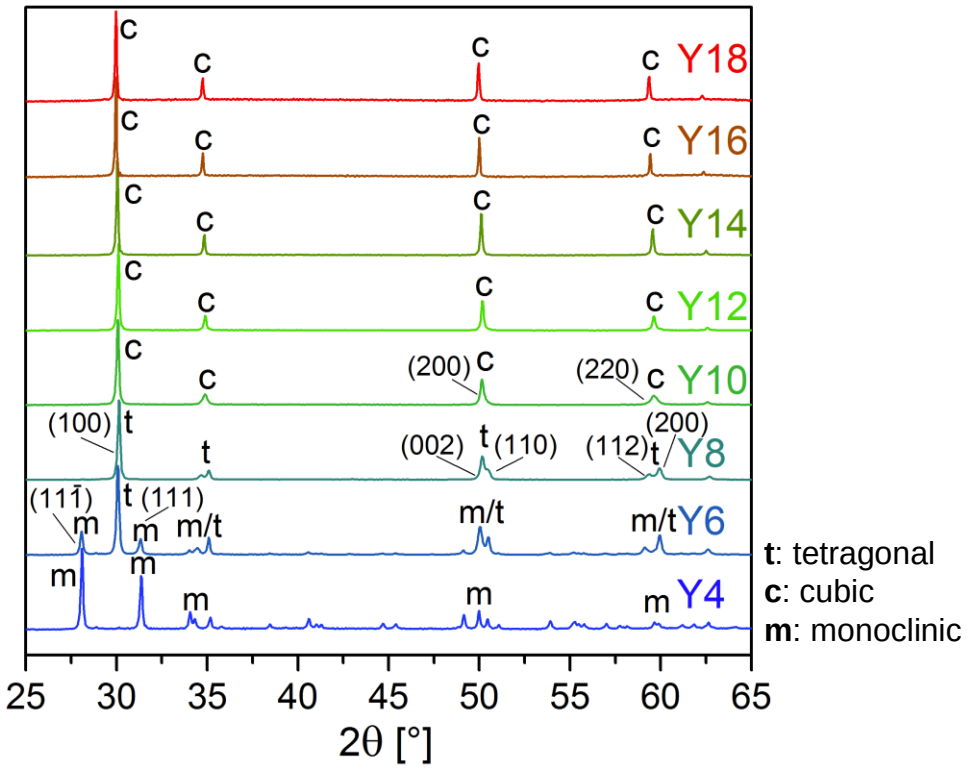
Temperature Stability of YSZ Investigated by Scanning Electron Microscopy

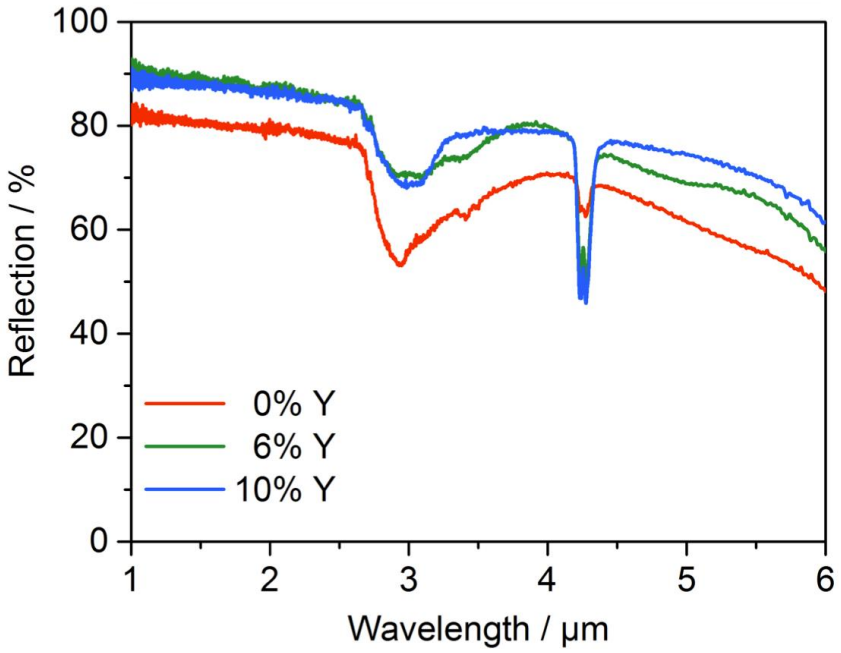


E. W. Leib *et al., J. Mater. Chem. C,* 4, 62-74, **2016**.

Y-Stabilized ZrO_2 Microparticles Show Broadband Reflection in the IR-Range

Crystal Structure and Optical Properties of YSZ after 1400 °C for 3 h





phase stabilization by Y-doping

broadband reflection in IR-range

E. W. Leib *et al., J. Mater. Chem. C,* 4, 62-74, **2016**.

Outline: Structural Colors (SC)

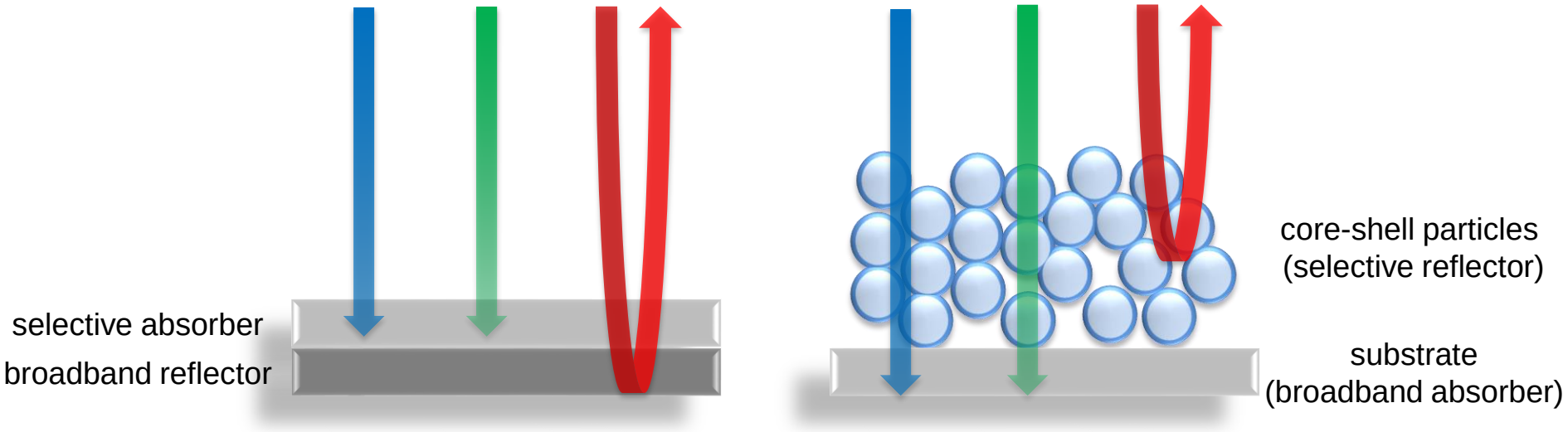


Pigmented Colors Selectively Absorbe Light, Structural Colors Selectively Reflect Light

Pigmented Color vs. Structural Color

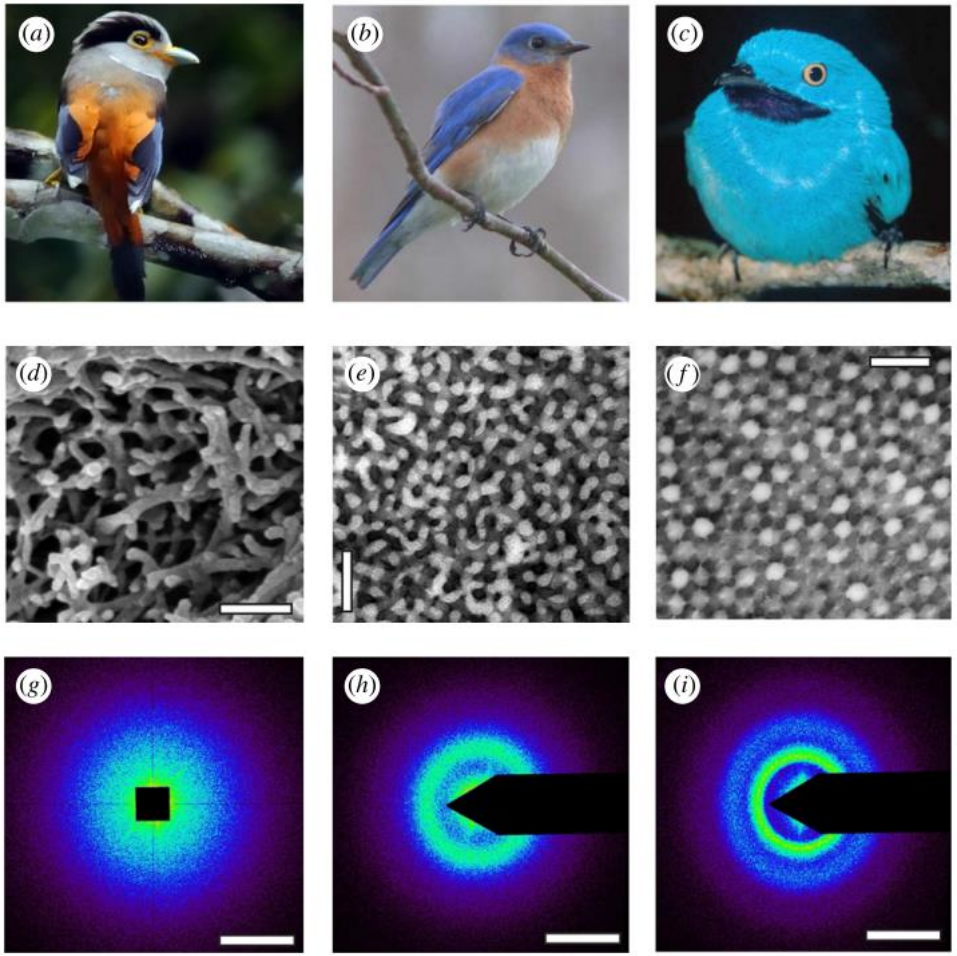
pigmented color

structural color



Bright Blue Structural Colors in Nature Exhibit Isotropy and Short-Range Periodicity of Nanostructures

Blue Colored Birds (a-c), SEM/TEM Images (d-f) and SAXS Images (g-i)



- diversity of non-iridescent feather barb structural colors in birds
- morphology of their underlying three-dimensional amorphous photonic nanostructures with short-range quasi-periodic order

Small-angle X-ray scattering (SAXS) patterns for channel- and sphere-type nanostructures exhibit ring-like features.

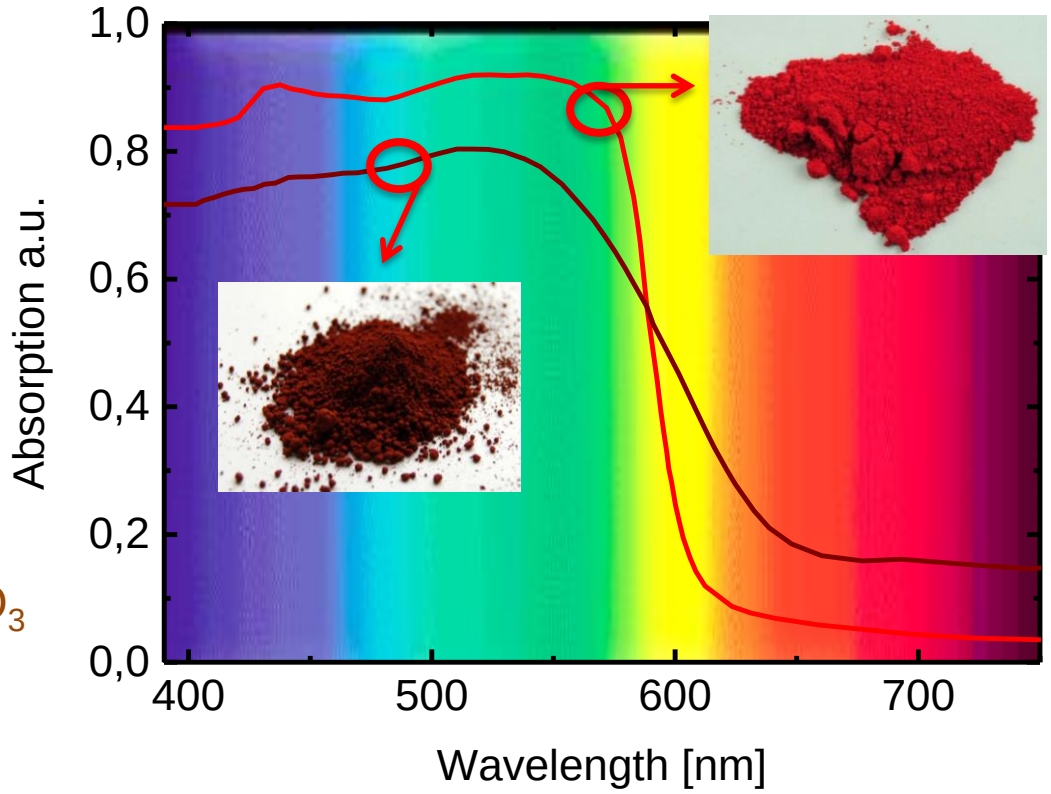
V. Saranathan *et al*., *J. R. Soc. Interface,* 9, 2563–2580, **2012**.

Hardly any High-Temperature Stable Highly Saturated Red and Orange Colors

Motivation: Structural Colors (SC)

toxic highly saturated red and orange colors for high-temperature application

→ **aim**: non-toxic and environmentally friendly colorants



$Cd(S_x,Se_{1-x})$

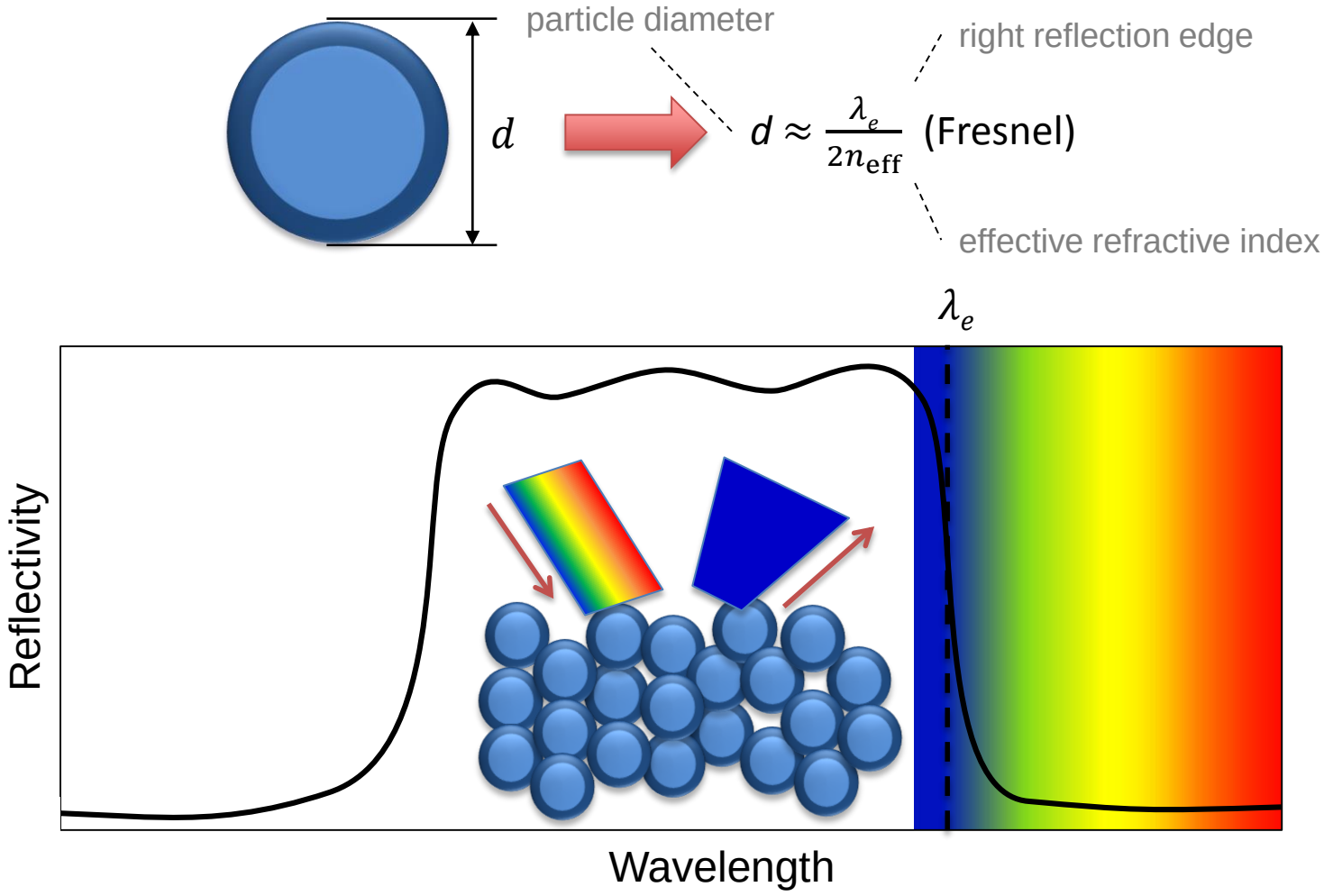
Cr-doped $YAlO_3$

P.M.T. Cavalcante *et al.*, *Dyes and Pigments*, **2009**.
Adopt from: D. Jalas *et al.*, *High temperature stable structural colors,* **2015**.

Reflection Spectrum dependent on Particle Diameter and Effective Refractive Index

Reflectivity: Fresnel Equation

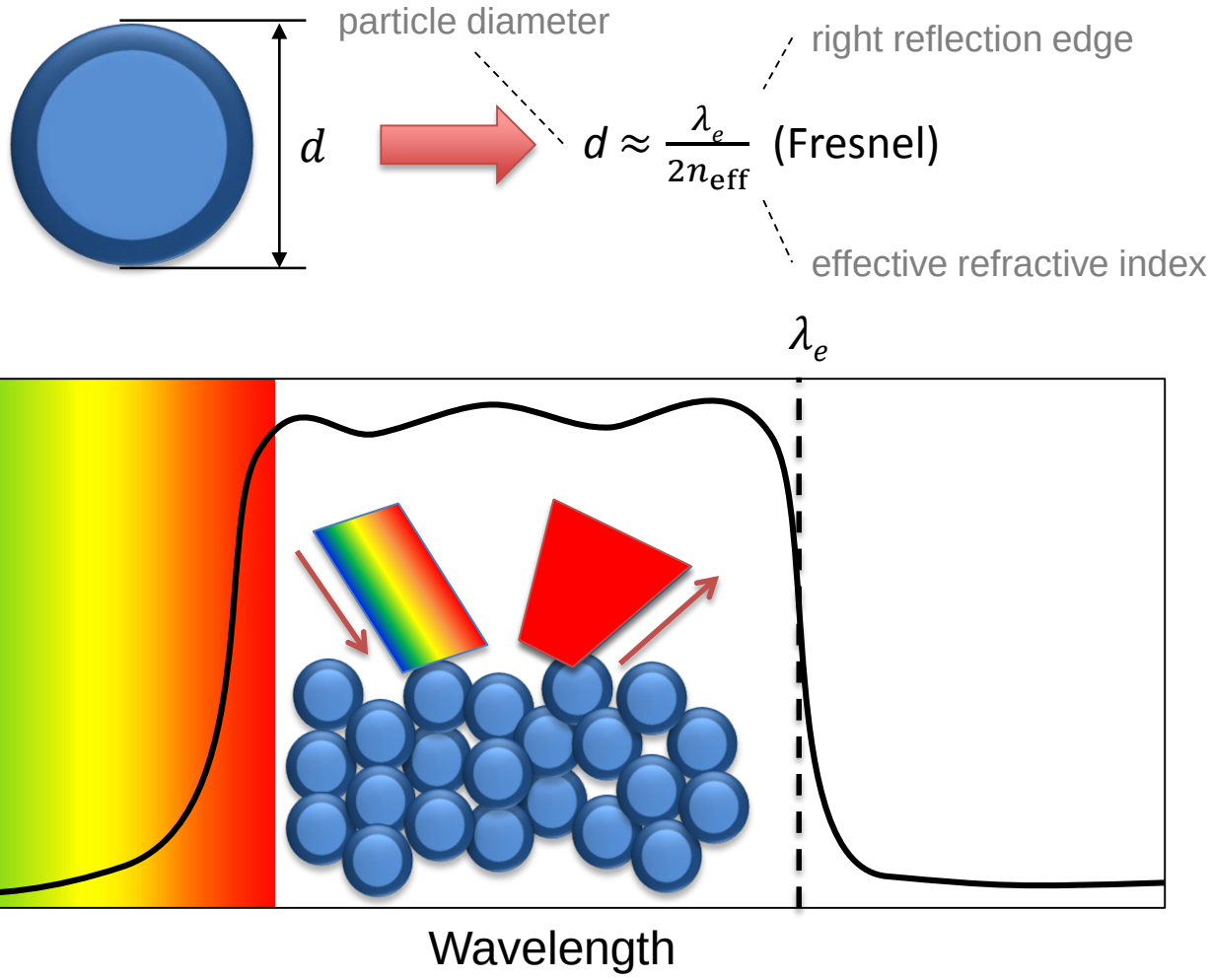
G. Meltz, W. W. Morey, W. H. Glenn, *Opt. Lett.*, *14*, 823-825, **1989**.



Reflection Spectrum dependent on Particle Diameter and Effective Refractive Index

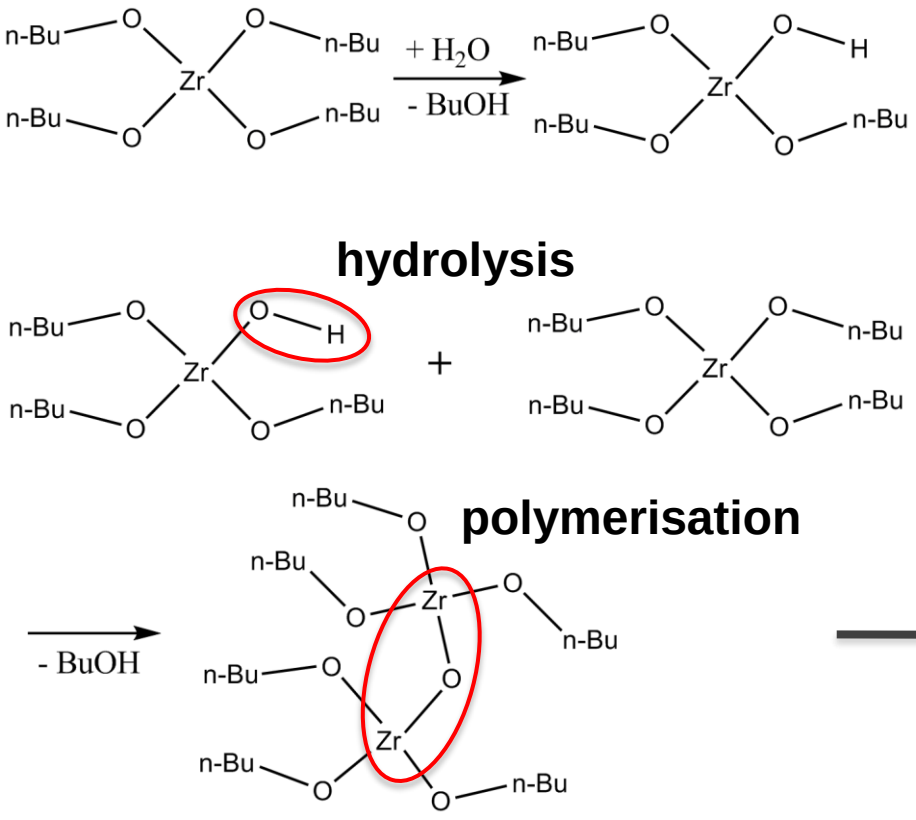
Reflectivity: Fresnel Equation

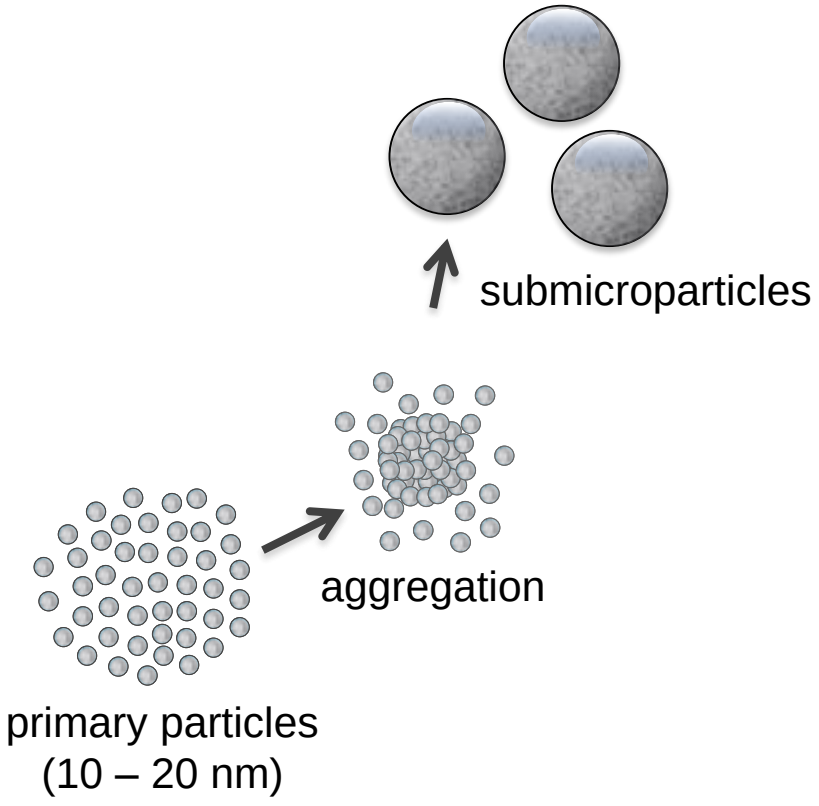
G. Meltz, W. W. Morey, W. H. Glenn, *Opt. Lett.*, *14*, 823-825, **1989**.



Sol-Gel Chemistry for Synthesis of Submicron ZrO_2 Core Particles

Core Synthesis: ZrO_2 Submicroparticles

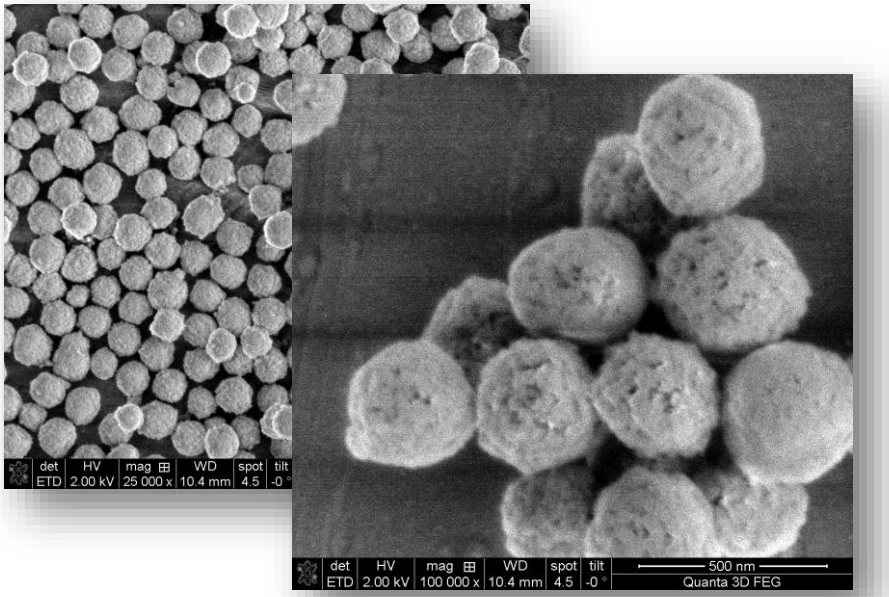




J. Widoniak *et al.*, *Eur. J. Inorg. Chem.*, 3149-3155, **2005**.
B. Yan *et al.*, *J. Am. Ceram. Soc.*, *88*, 707-713, **2005**.

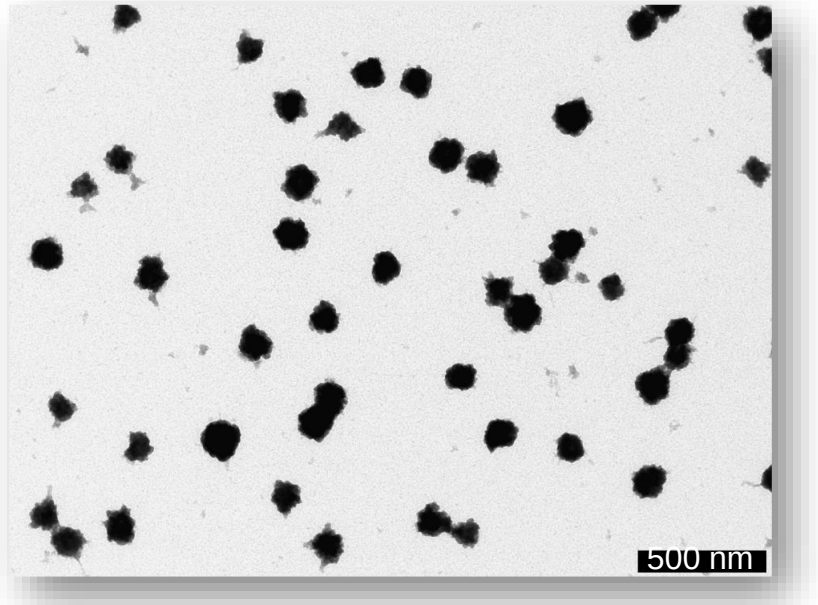
Particle Size Reduction Leads to Rougher Surface and Larger Size Distributions

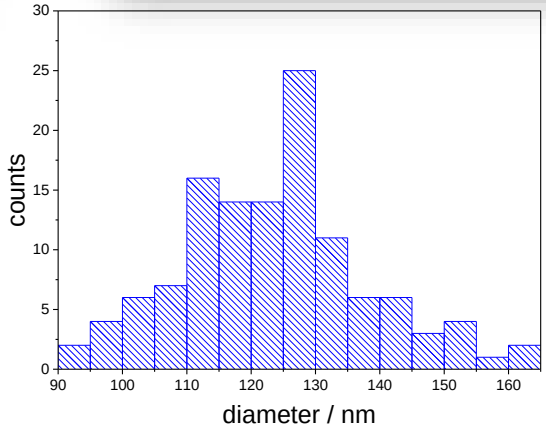
Characterization: Scanning/Transmission Electron Microscopy (SEM/TEM)



SEM:
undoped ZrO_2 particles

***d* = 421 nm ± 7 %**





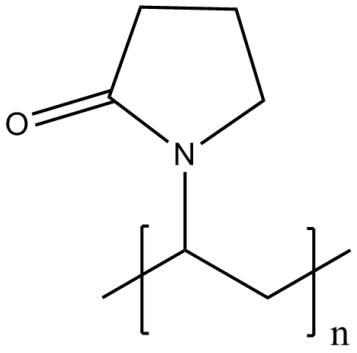
TEM:
YSZ particles

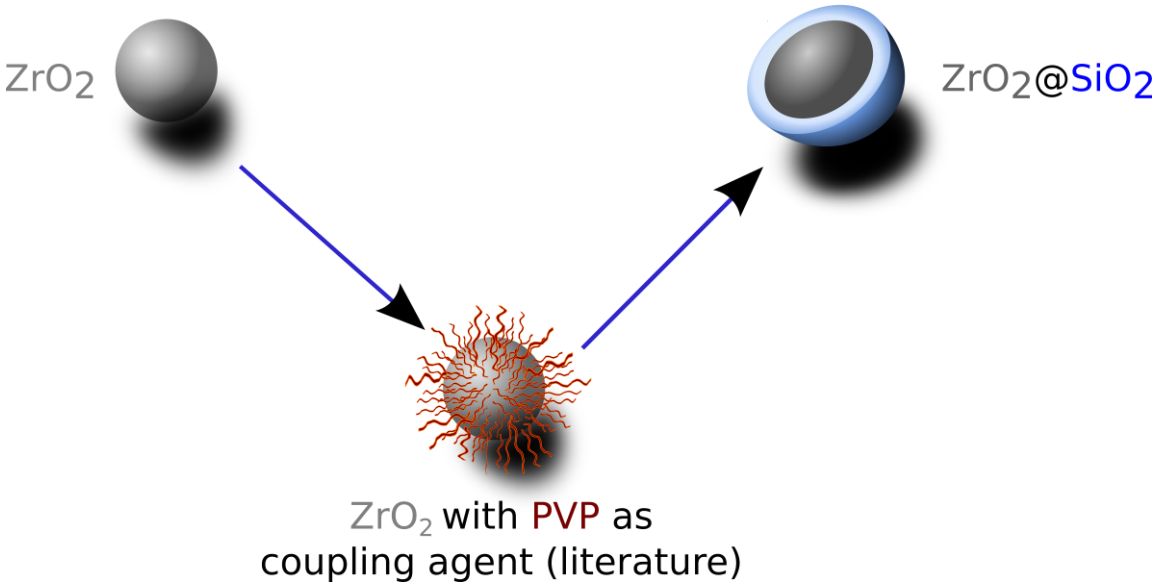
***d* = 123 nm ± 12 %**

Literature-Known Synthesis of Silica-Shell by using Coupling Agents

Core-Shell Synthesis: ZrO_2@SiO_2 Particles

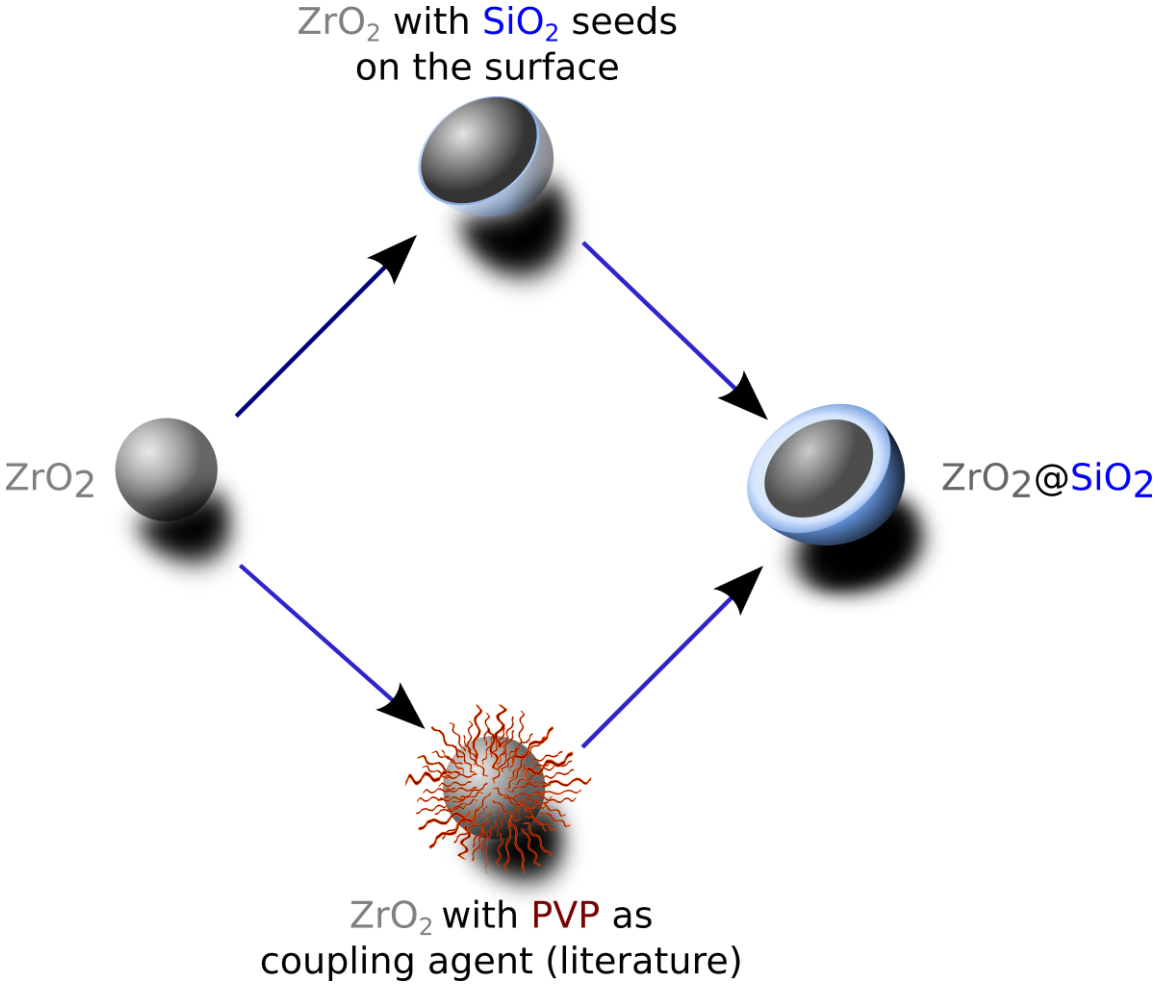
PVP: Polyvinylpyrrolidone





Encapsulation with Silica by using Self-Adhesive Silica Seeds

Core-Shell Synthesis: ZrO_2@SiO_2 Particles





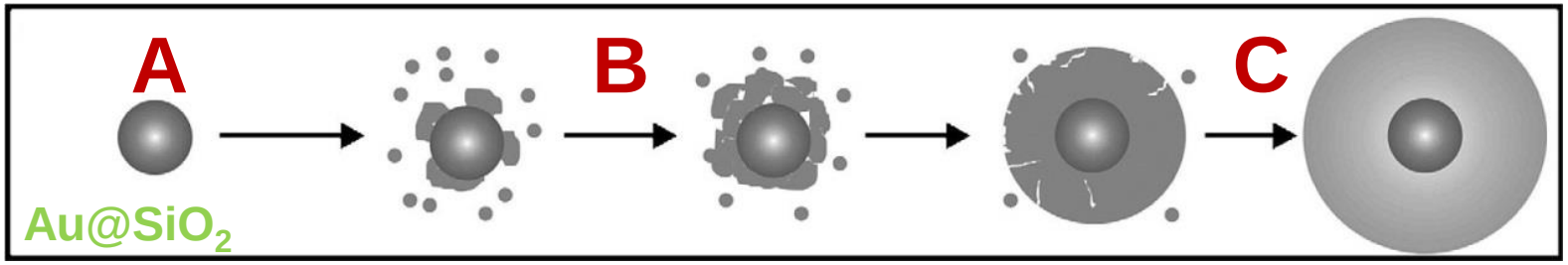


Stepwise Growth of a Smooth Silica-Shell

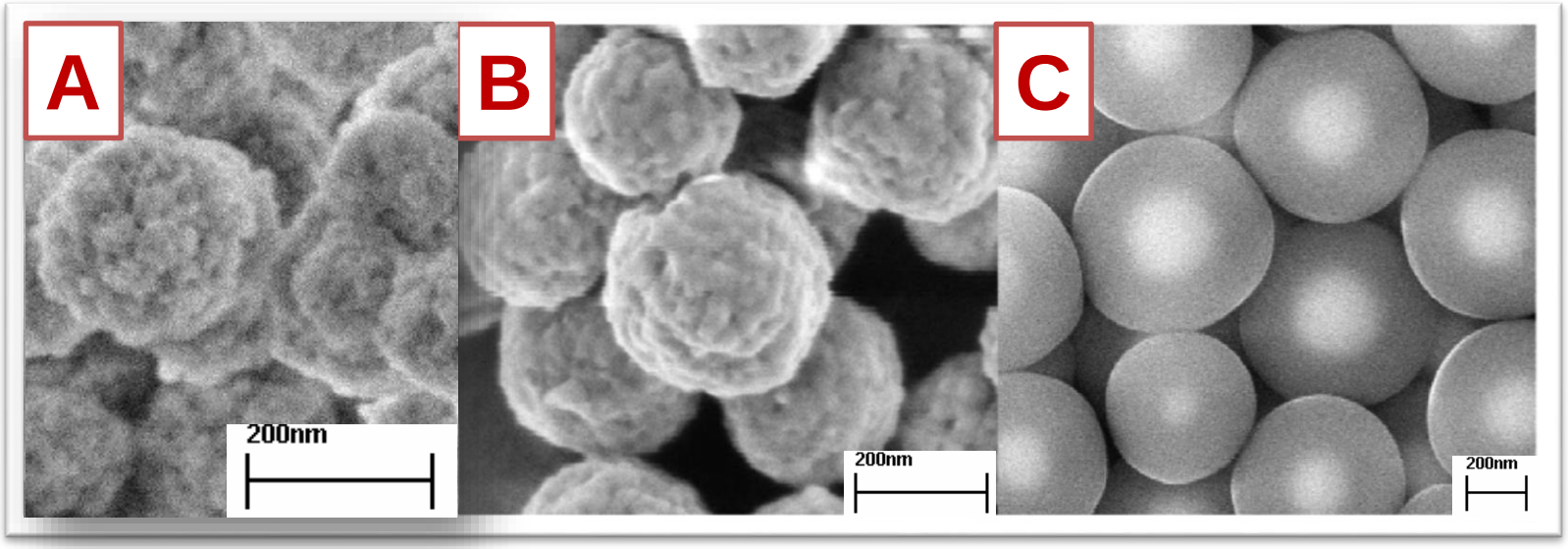
Mechanism of Silica-Shell growth

Van de Broek, De Palma, Libaers, Clays, Van Roy, Borghs, Maes, *Colloids and Surfaces*, **2008**.

In literature: silica-shell growth on gold nanoparticles



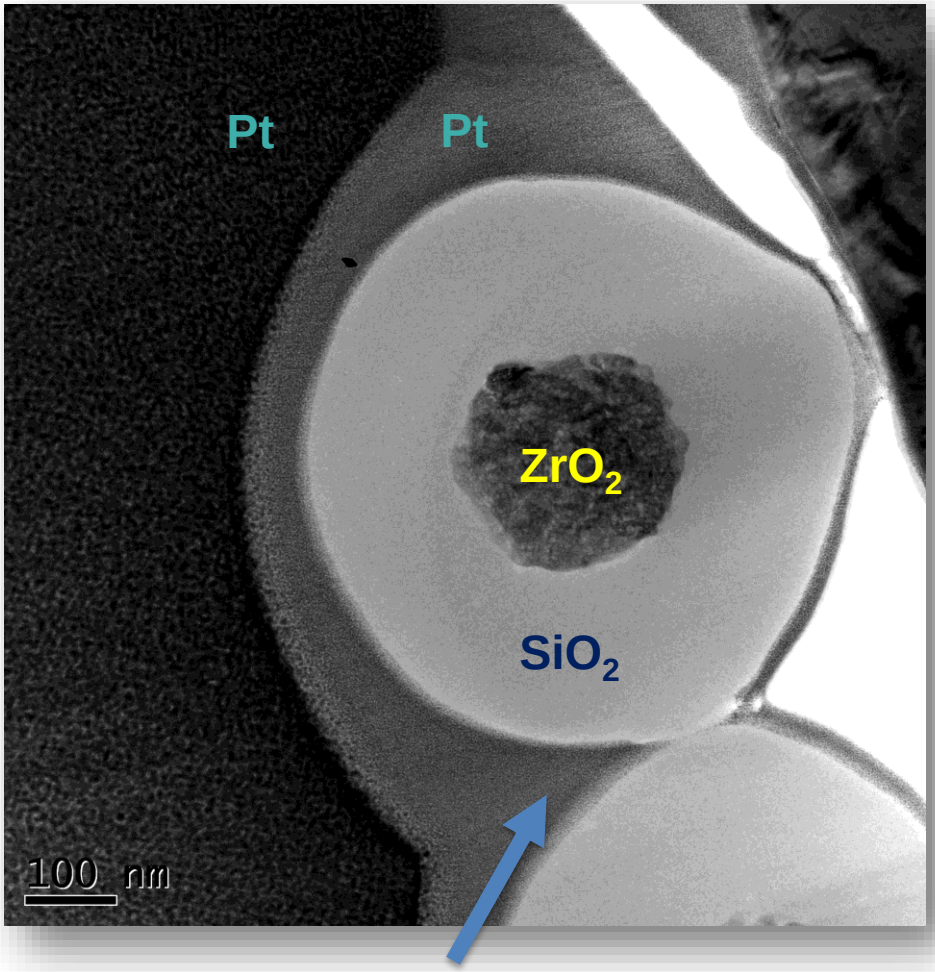
In our synthesis: silica-shell growth on zirconia submicroparticles



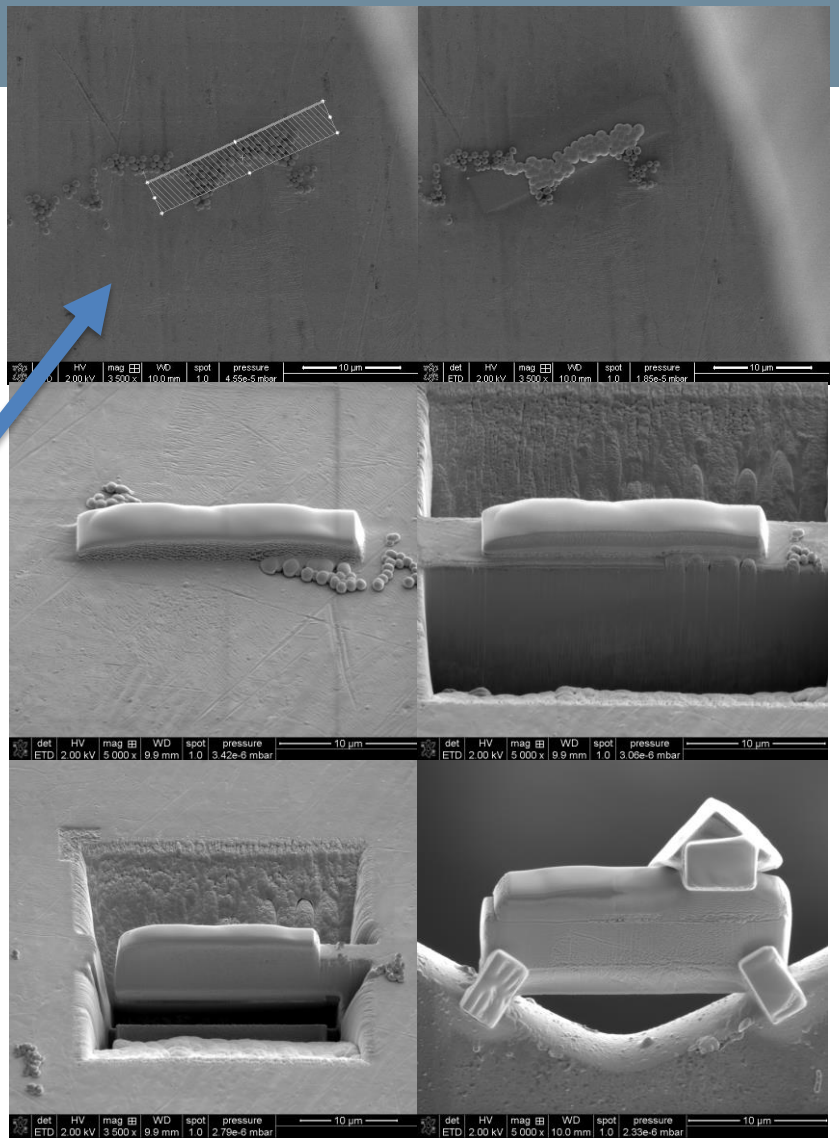
ZrO_2 ZrO_2 (SiO_2 seeds) $ZrO_2@SiO_2$

Core-Shell Structure Visible in TEM after Focused Ion Beam Lamella Preparation

Characterization: Focused Ion Beam (FIB)



SEM

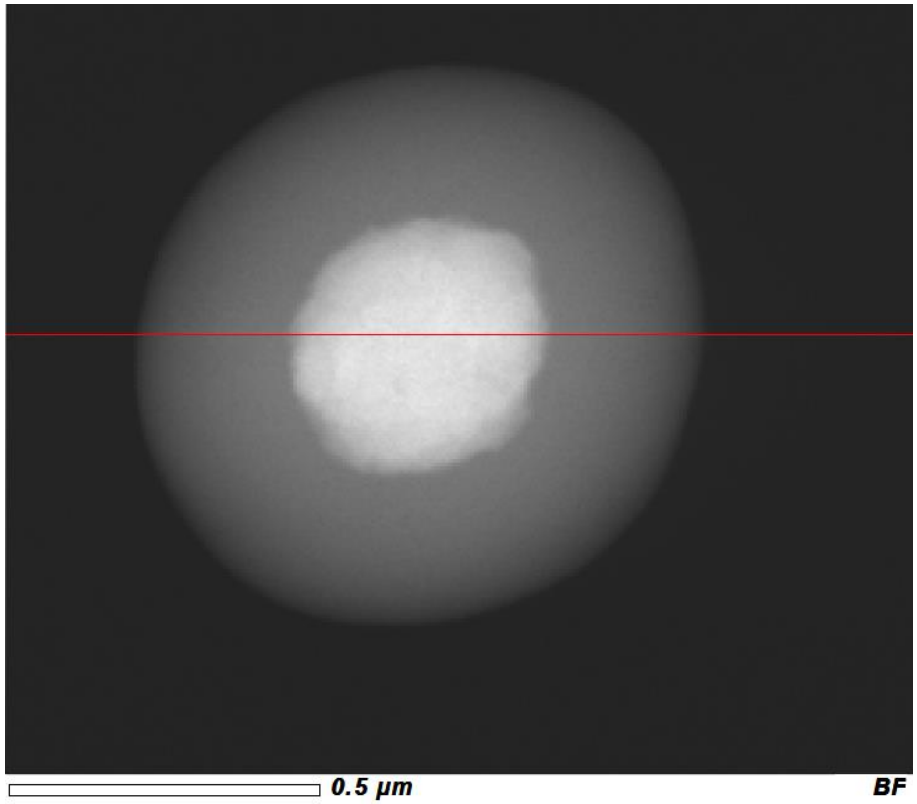


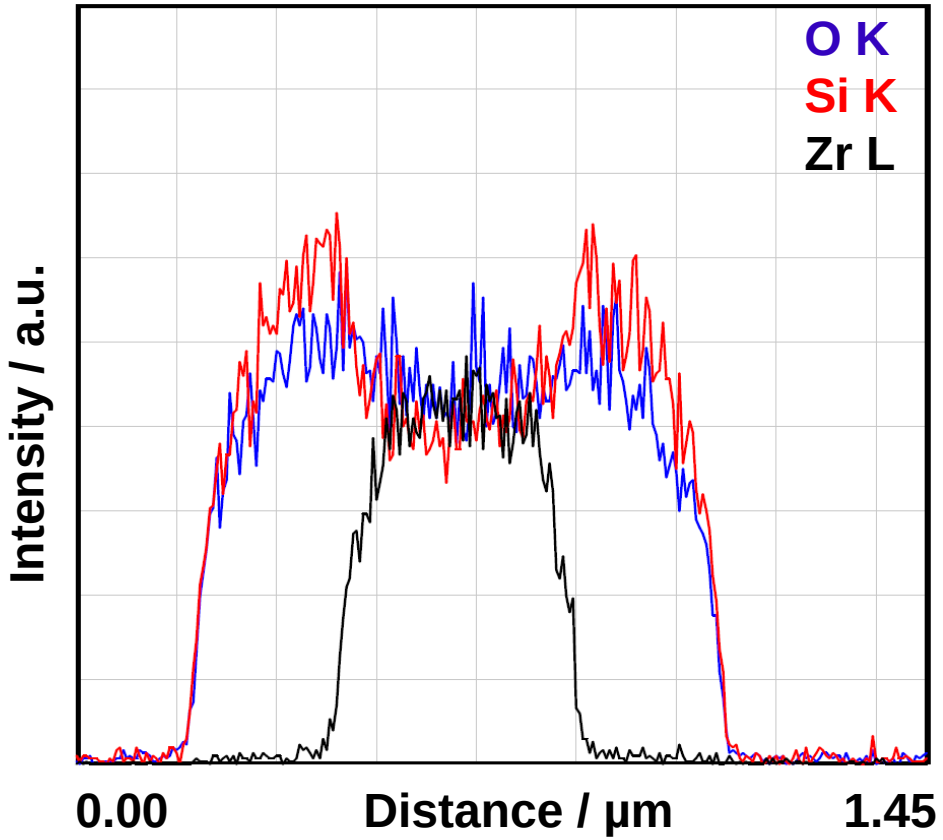
TEM Lamella of ZrO_2@SiO_2

Spectroscopic Investigations Confirmed ZrO_2@SiO_2 Core-Shell Structure

Characterization: Energy Dispersive X-Ray Spectroscopy (EDX)

- TEM-EDX analysis by a line scan

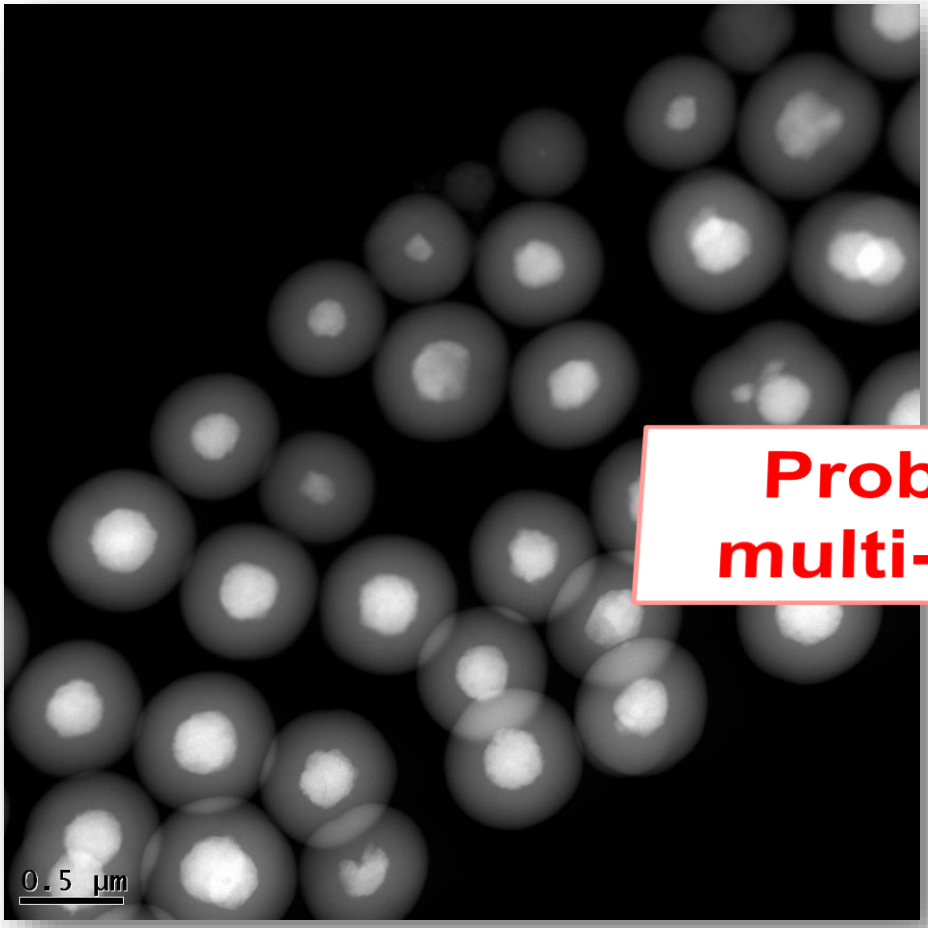


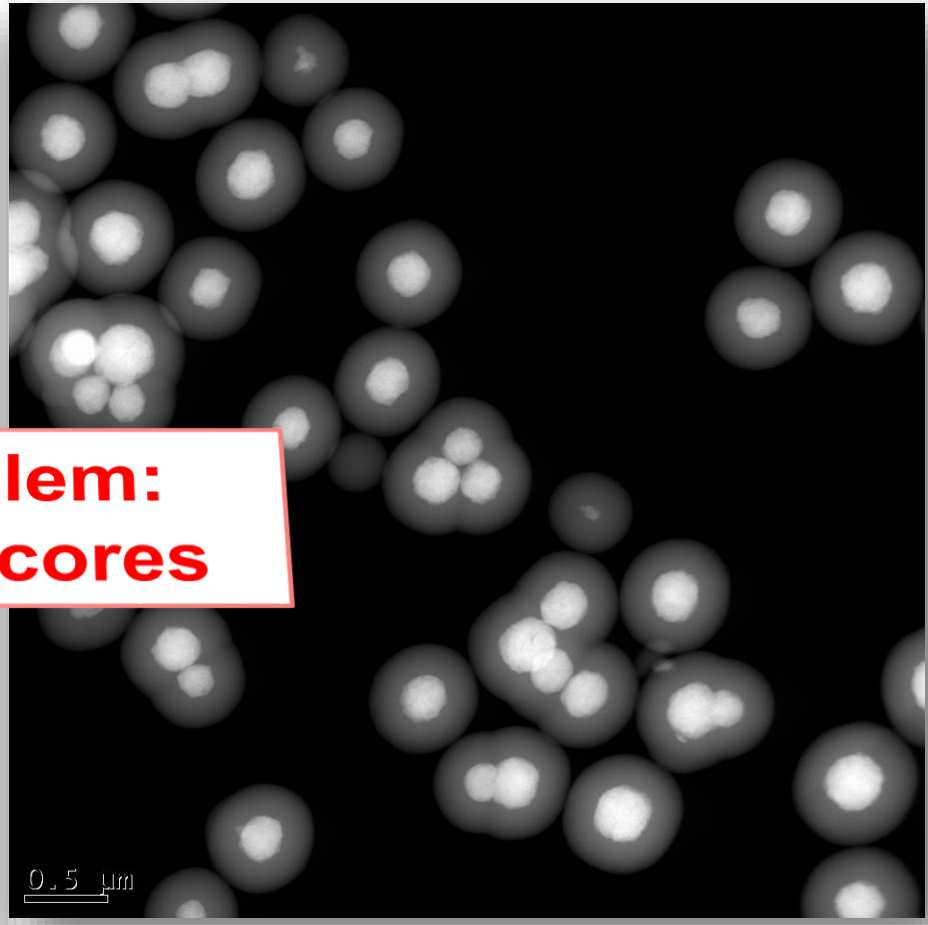


Multi-Cores occur during Synthesis without Coupling Agents

Characterization: Transmission Electron Microscopy (TEM)

- double- and multi-ZrO_2-cores: NH_3 concentration and coupling agents are crucial
  - ➢ pH = 10 - 11

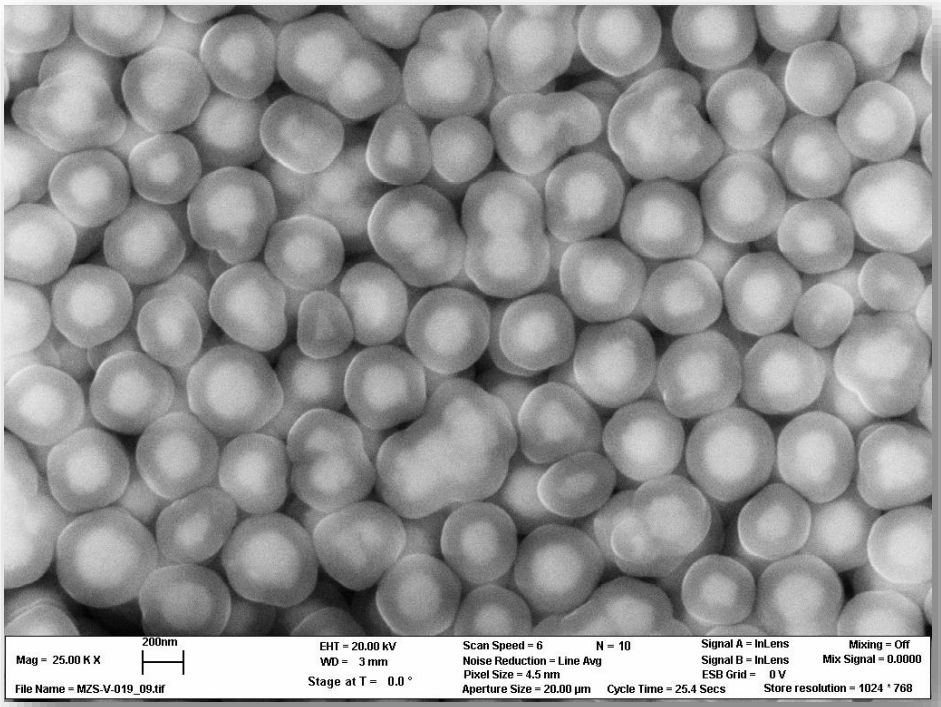


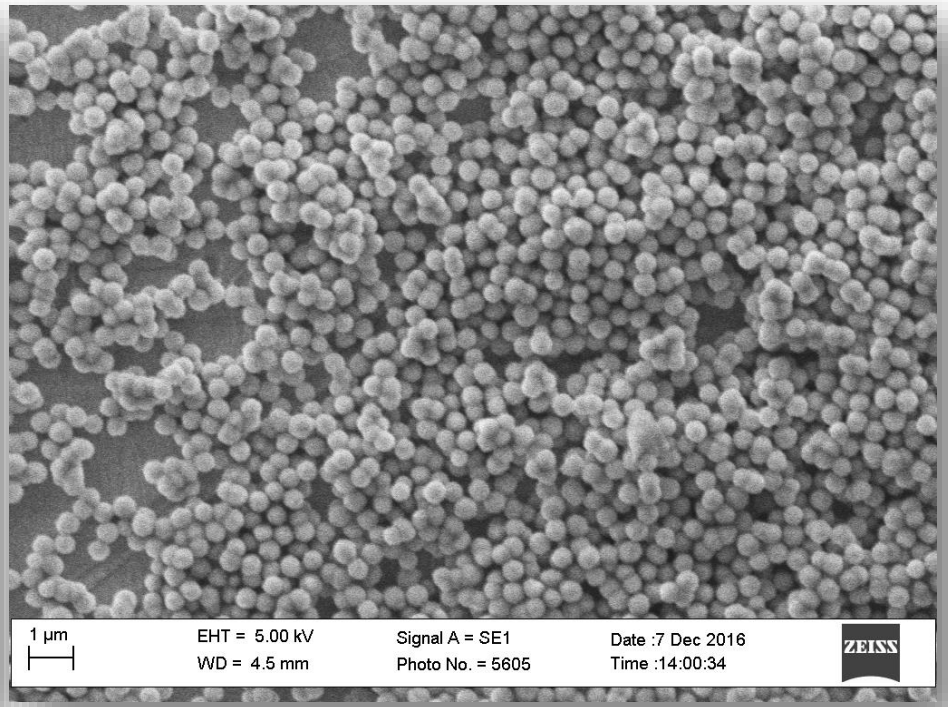


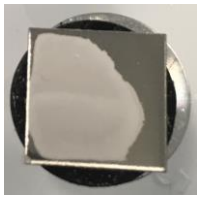
Problem: multi-cores

Multi-Cores can be Separated from Mono-Cores by Size-Selective Centrifugation

Characterization: Scanning Electron Microscopy (SEM)

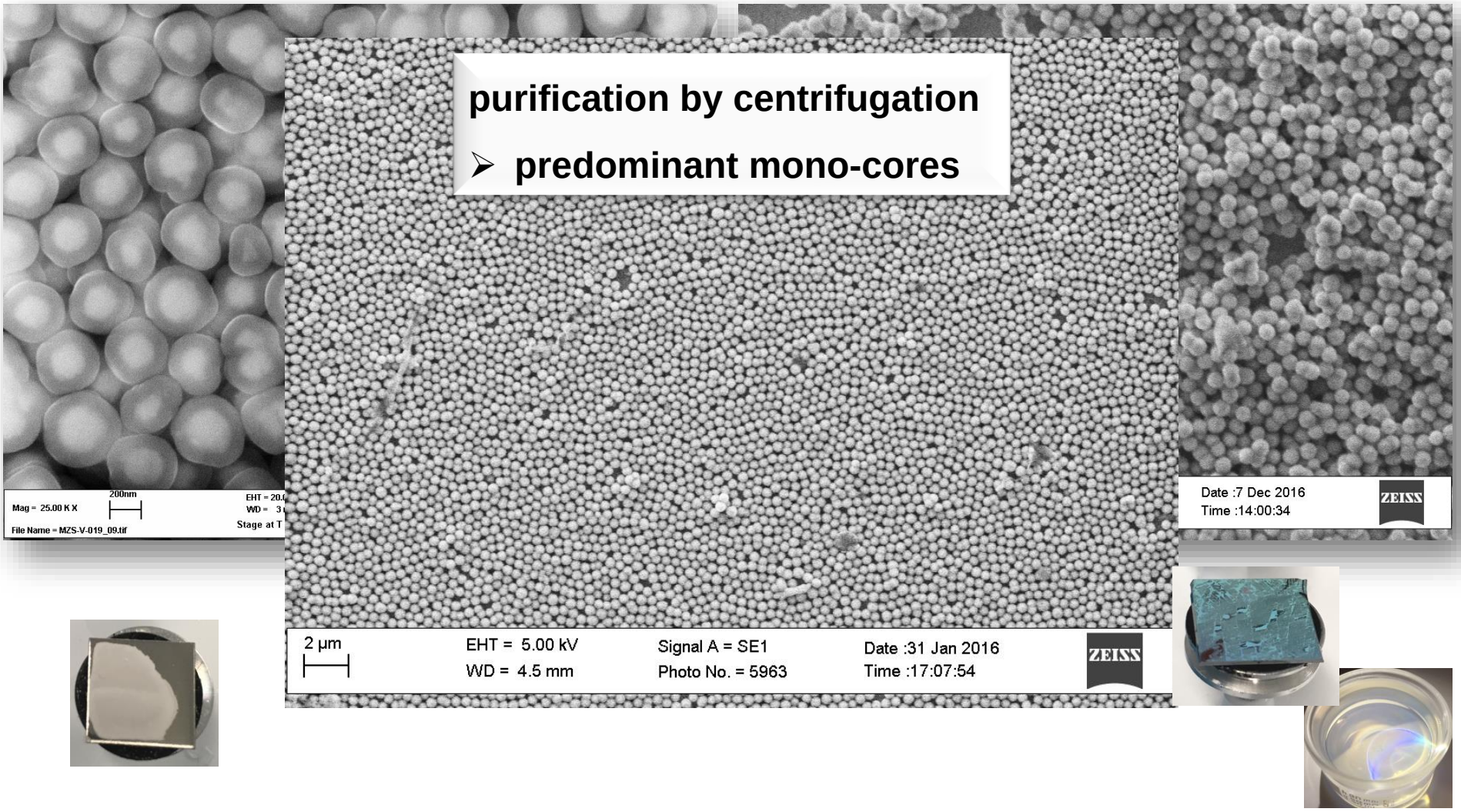






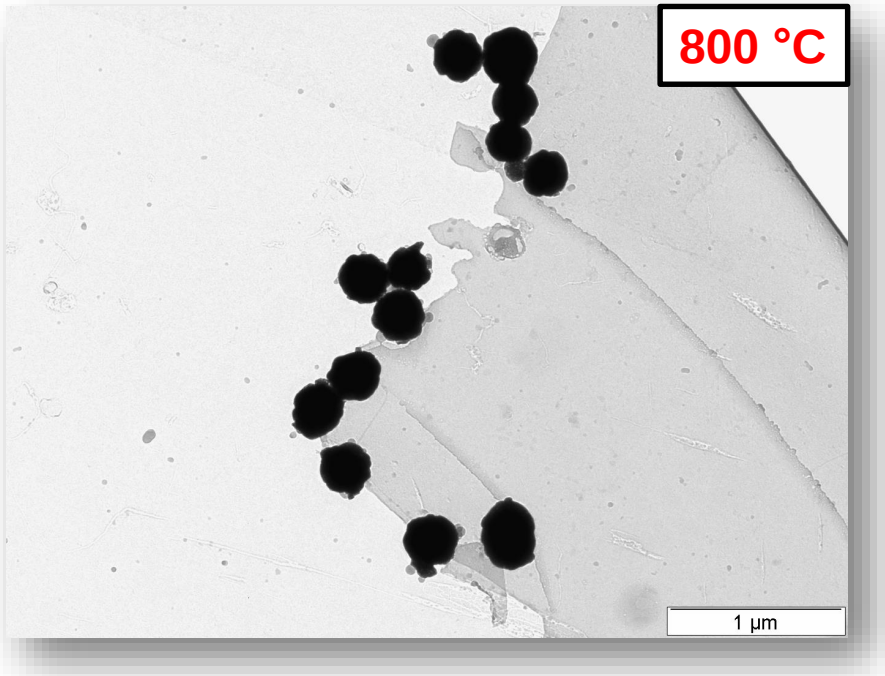
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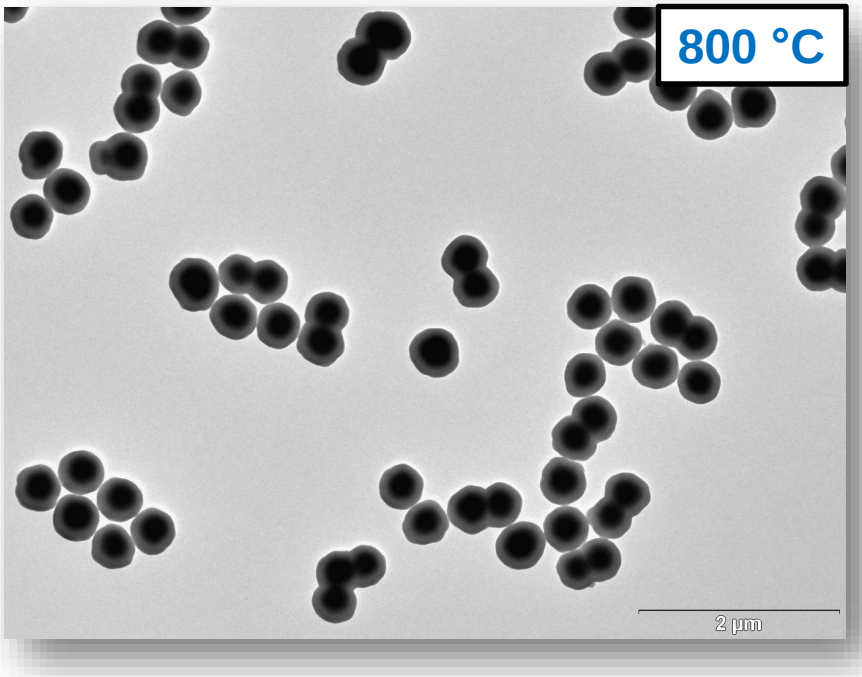


Improved Temperature Stability of Silica-Encapsulated Zirconia Submicroparticles

Temperature Stability: ZrO_2 Particles vs. ZrO_2@SiO_2 Core-Shell Partciles



TEM



ZrO_2

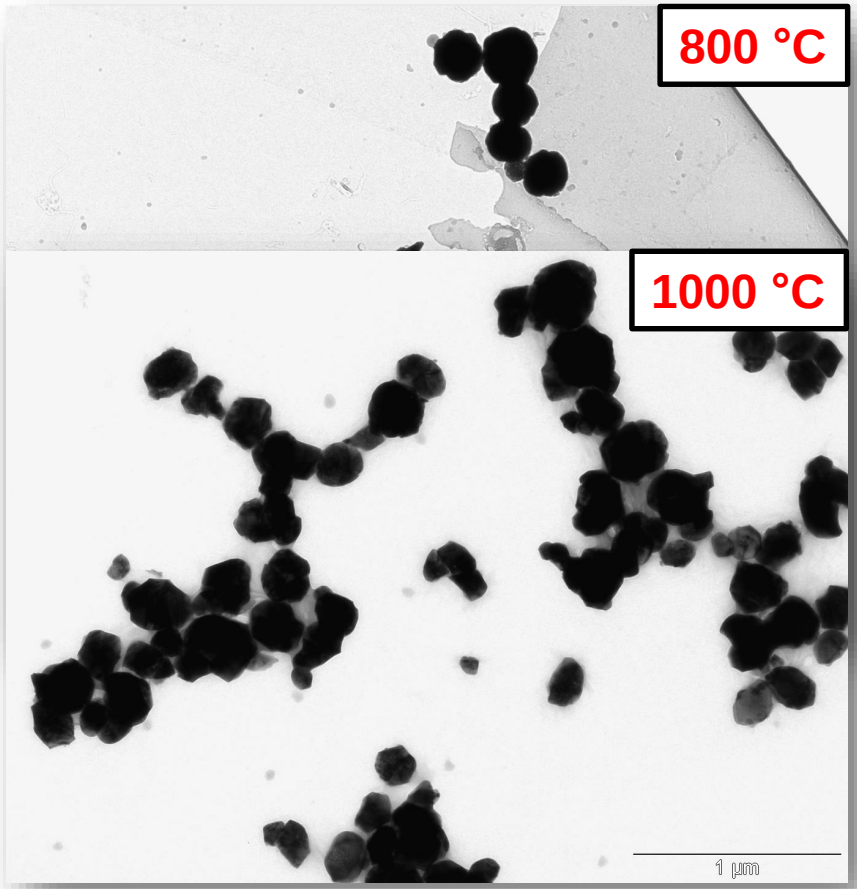
d_{core} = 421 ± 31 nm (~7 %)

ZrO_2@SiO_2

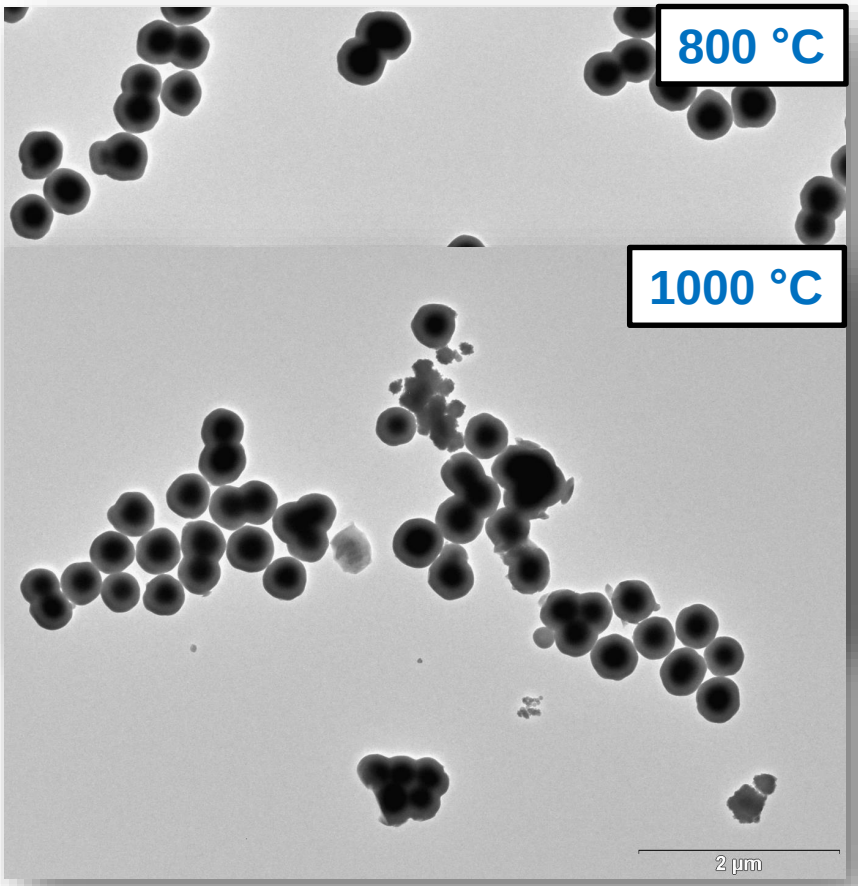
$d_{core\text{-}shell}$ = 469 ± 25 nm (~5 %, 76 nm shell)

Improved Temperature Stability of Silica-Encapsulated Zirconia Submicroparticles

Temperature Stability: ZrO_2 Particles vs. ZrO_2@SiO_2 Core-Shell Partciles



TEM



ZrO_2

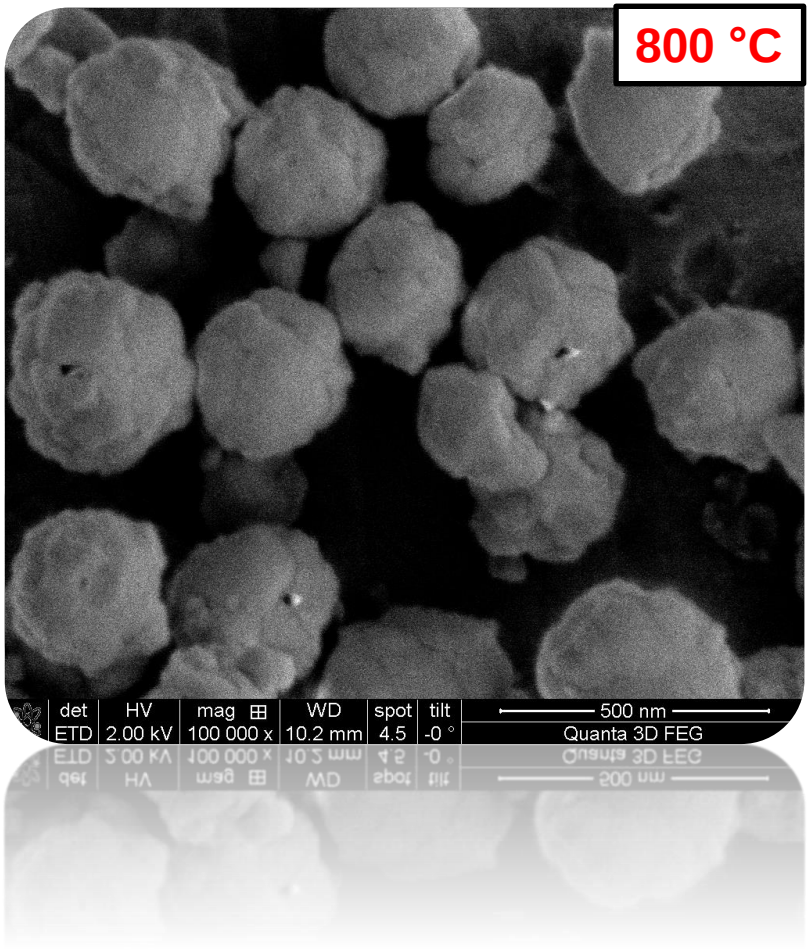
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ZrO_2@SiO_2

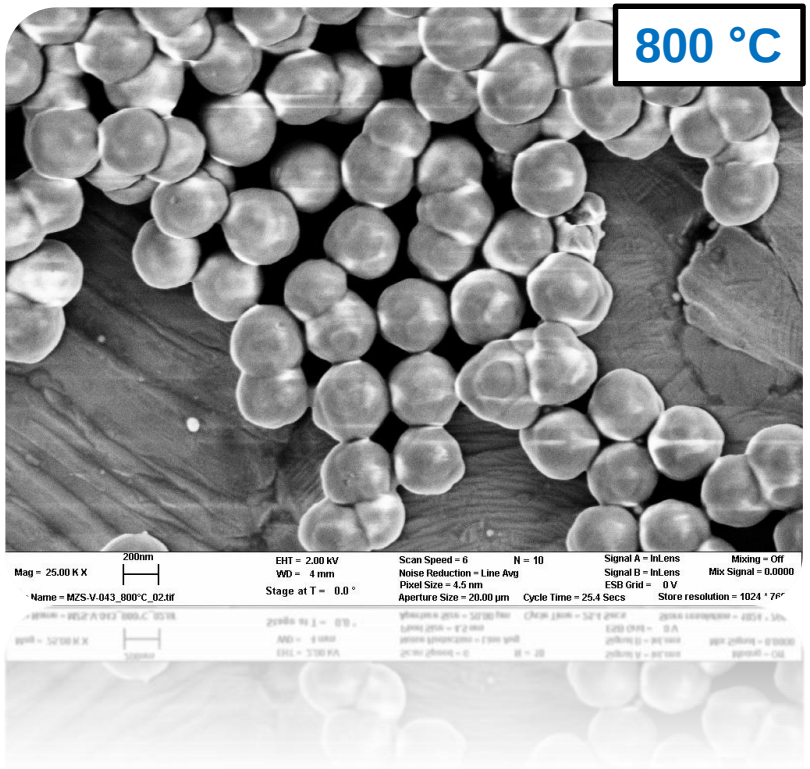
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Temperature Stability: ZrO_2 Particles vs. ZrO_2@SiO_2 Core-Shell Partciles



SEM

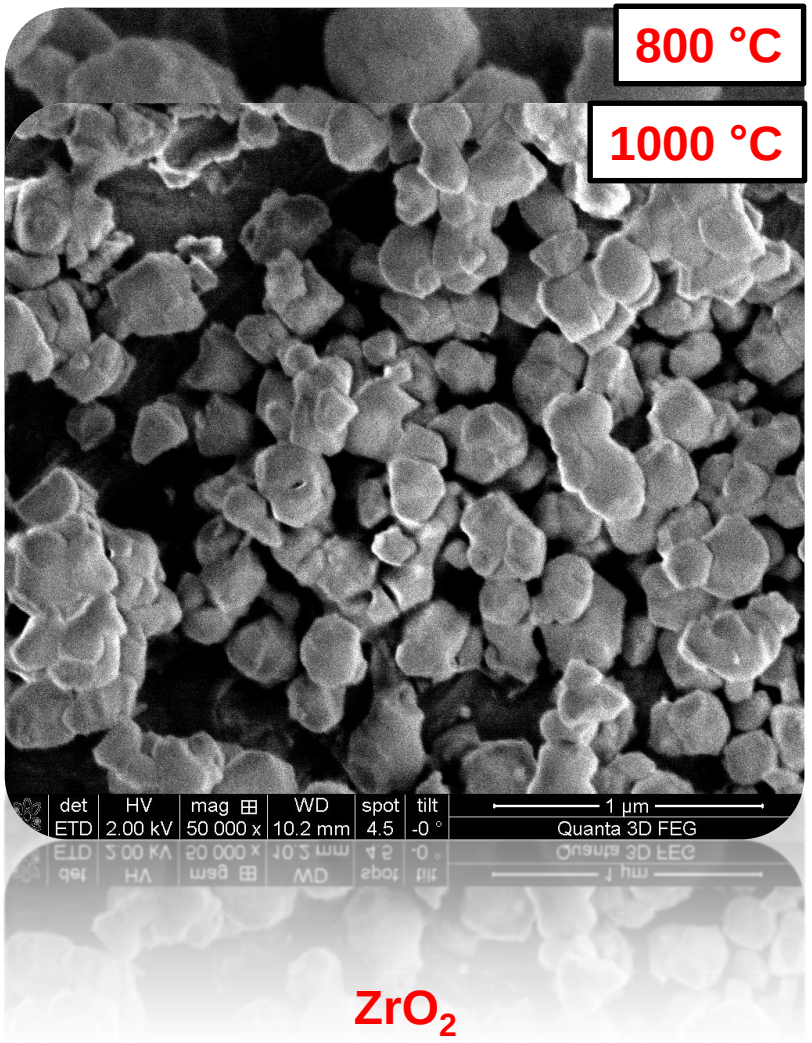


ZrO_2

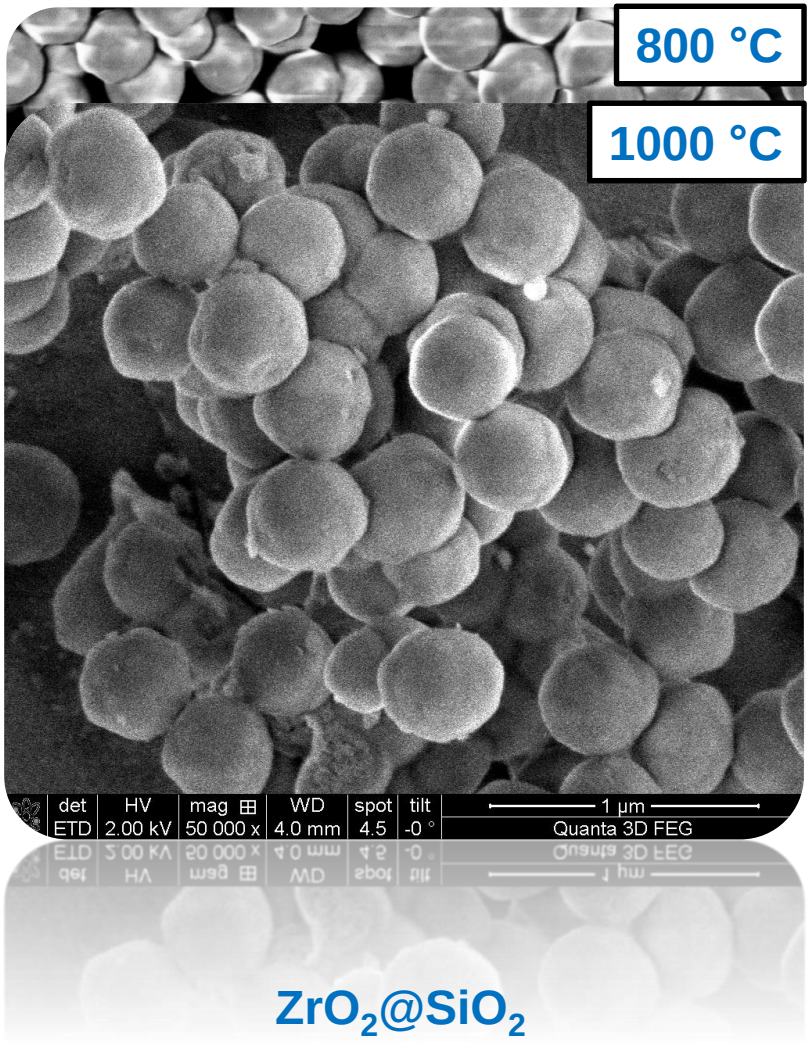
ZrO_2@SiO_2

Improved Temperature Stability of Silica-Encapsulated Zirconia Submicroparticles

Temperature Stability: ZrO_2 Particles vs. ZrO_2@SiO_2 Core-Shell Partciles



SEM

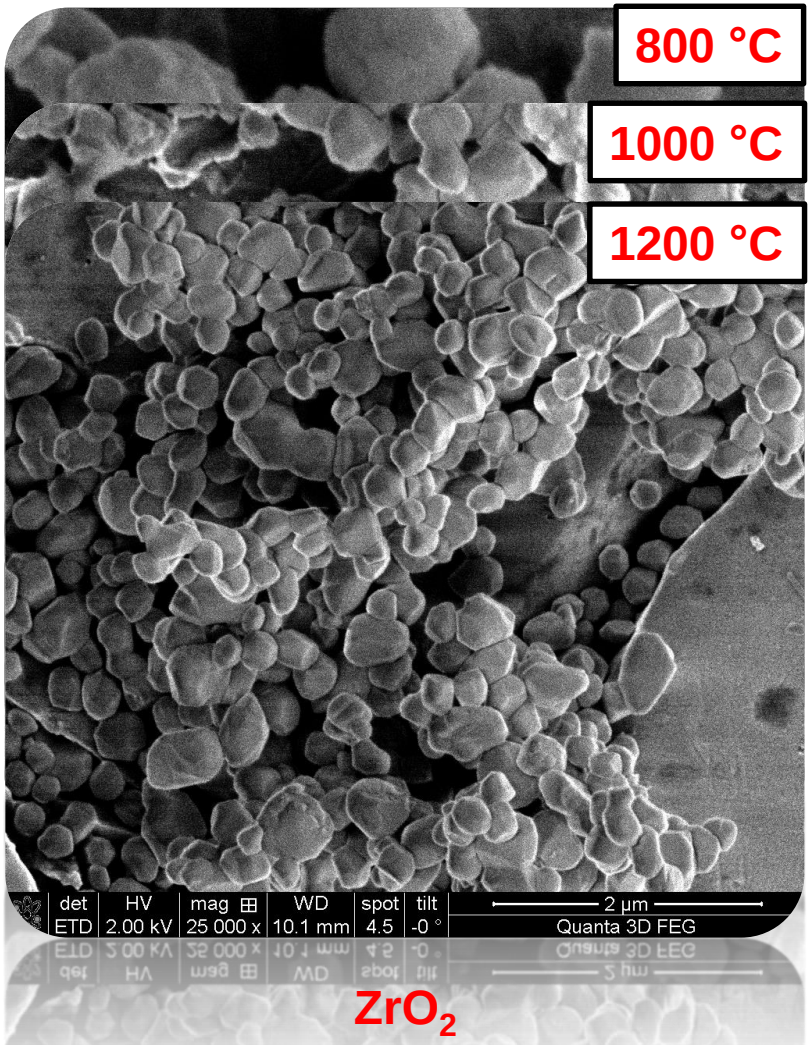


ZrO_2

ZrO_2@SiO_2

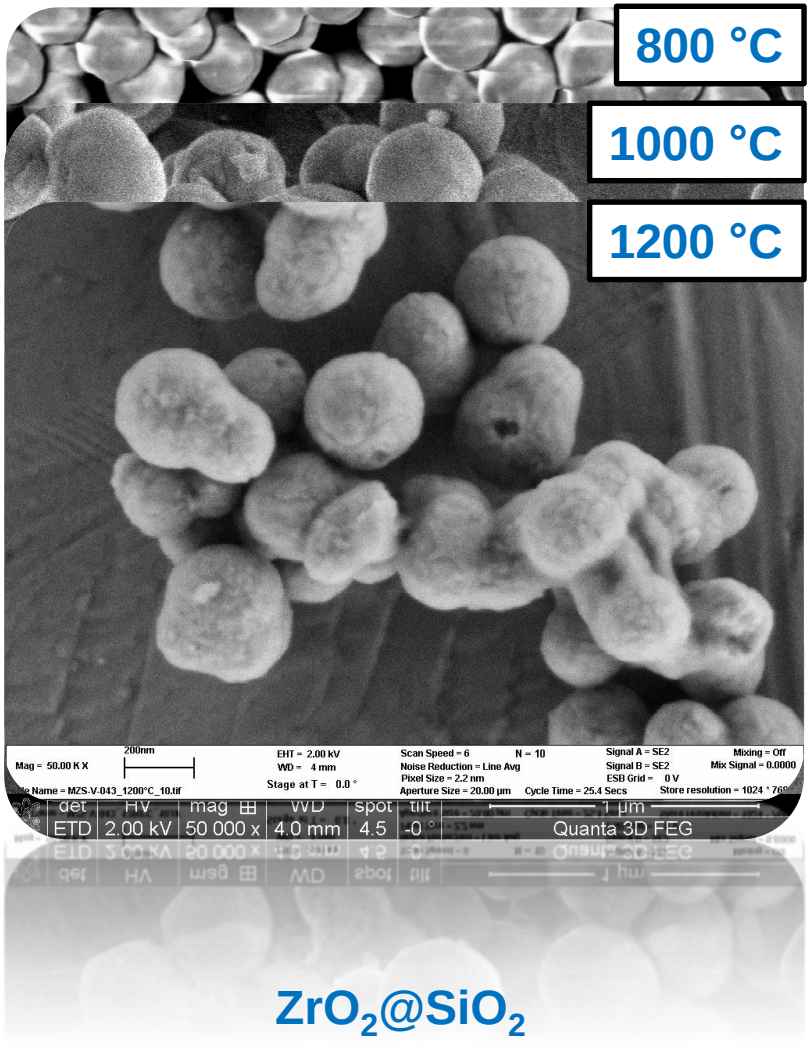
Improved Temperature Stability of Silica-Encapsulated Zirconia Submicroparticles

Temperature Stability: ZrO_2 Particles vs. ZrO_2@SiO_2 Core-Shell Partciles



ZrO_2

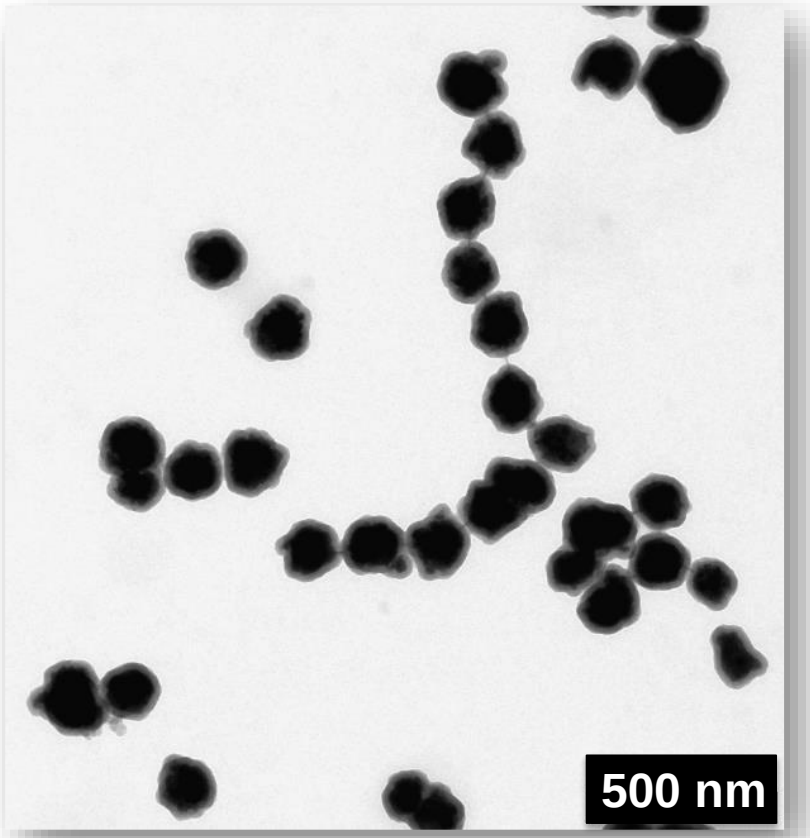
SEM



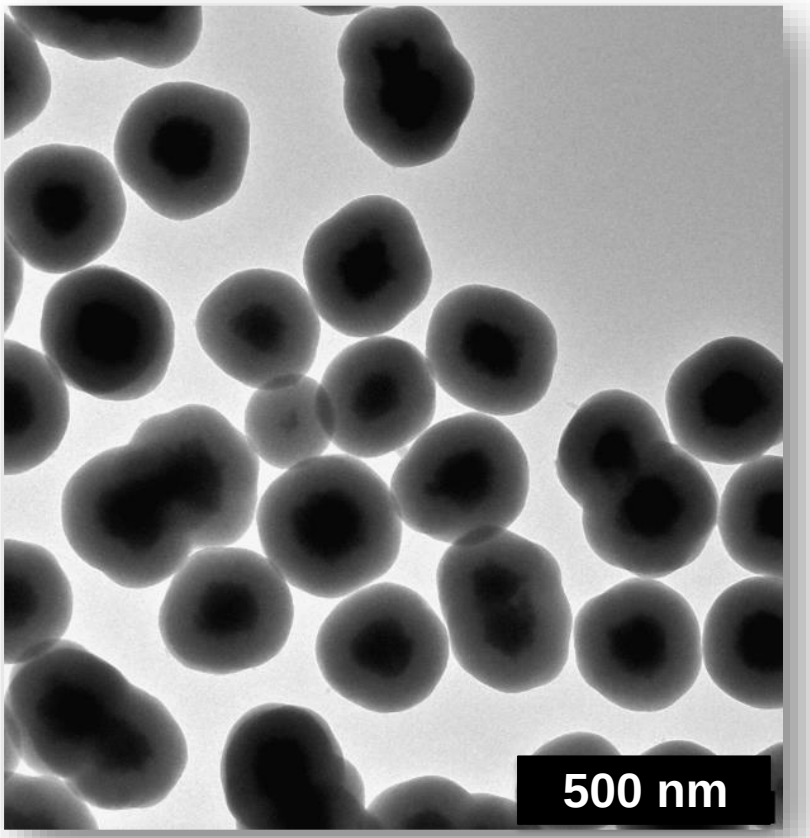
ZrO_2@SiO_2

Synthesis of the Target Core-Shell Particle Size with a Smooth Surface is still in Progress

TEM Images of ZrO_2@SiO_2 Core-Shell Particles for Structural Colors



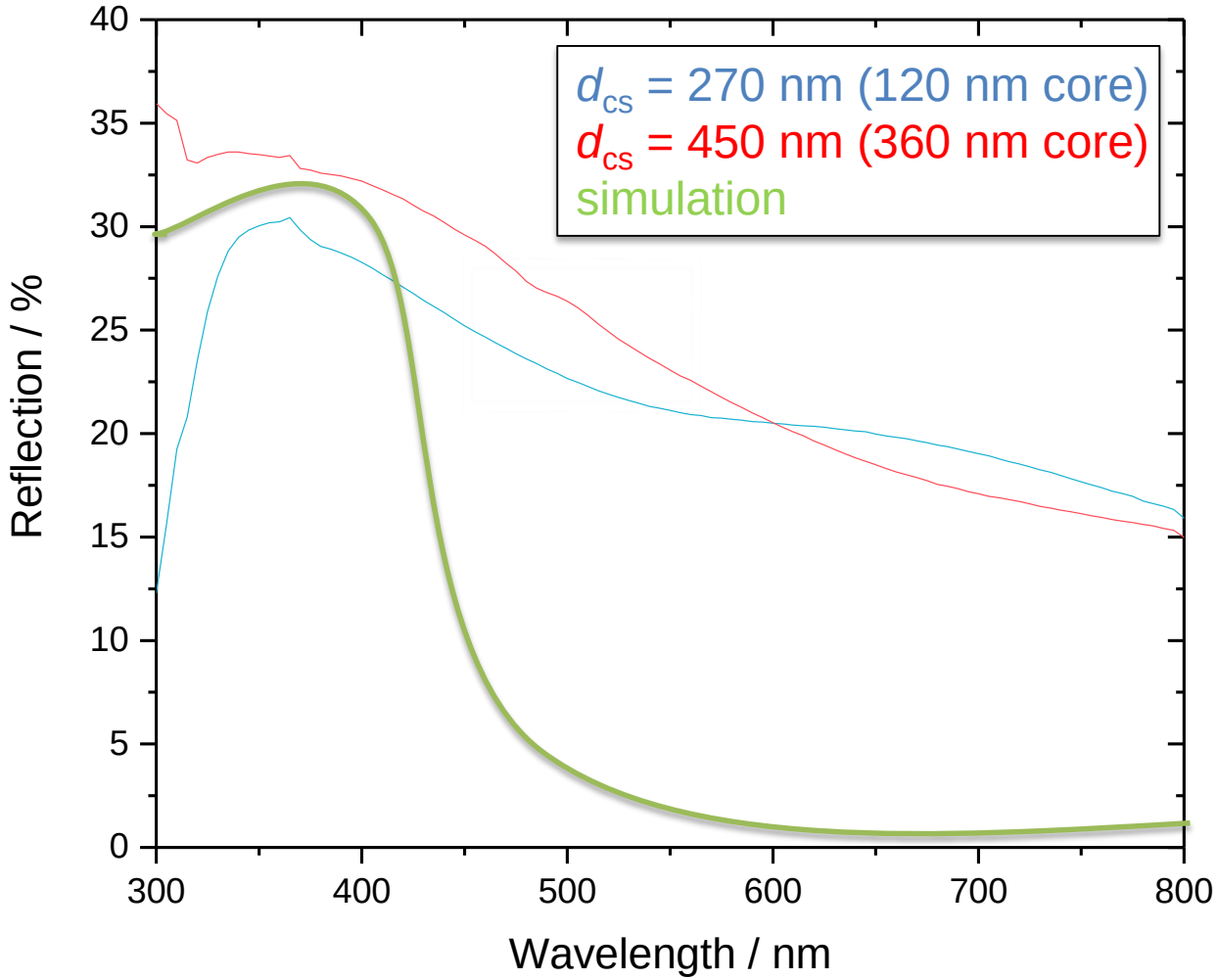
$d_{core\text{-}shell}$ = 172 nm ± 9 %



$d_{core\text{-}shell}$ = 272 nm ± 8 %

Sharper Reflection Edge is Needed by Reducing the Core-Shell Size and Dispersity

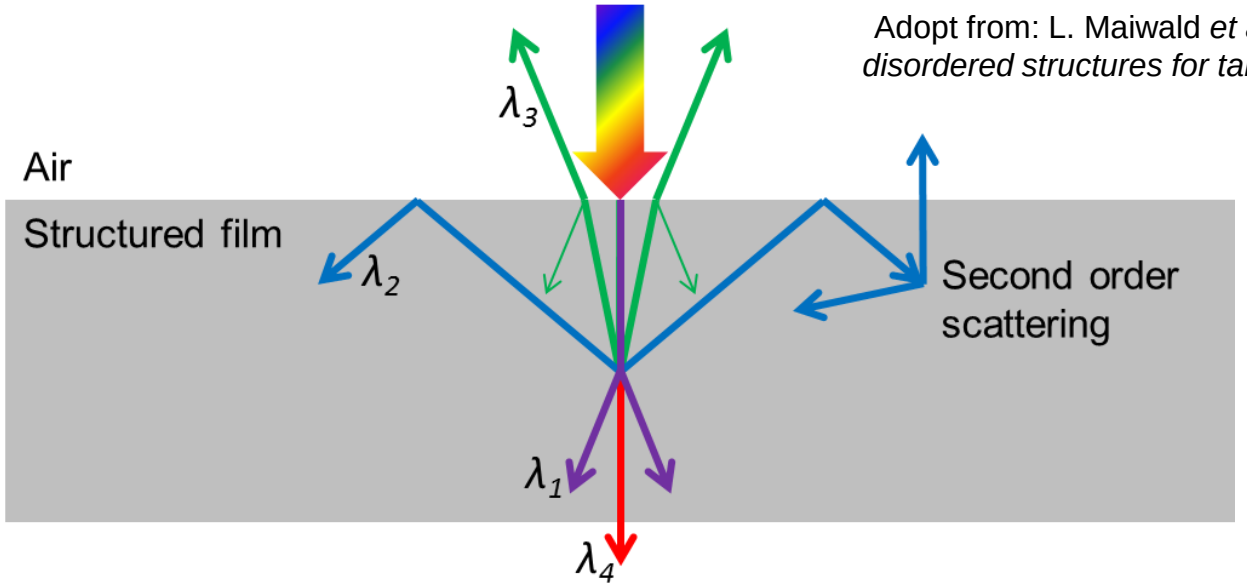
Optical Properties of ZrO_2@SiO_2 Photonic Glasses

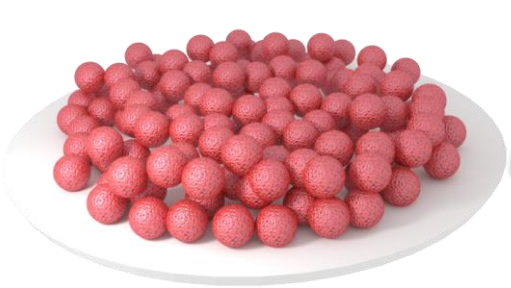


Sharper Reflection Edge by Introducing an Absorbing Matrix

Outlook

Adopt from: L. Maiwald *et al.*, *Holography based disordered structures for tailored scattering,* **2015**.





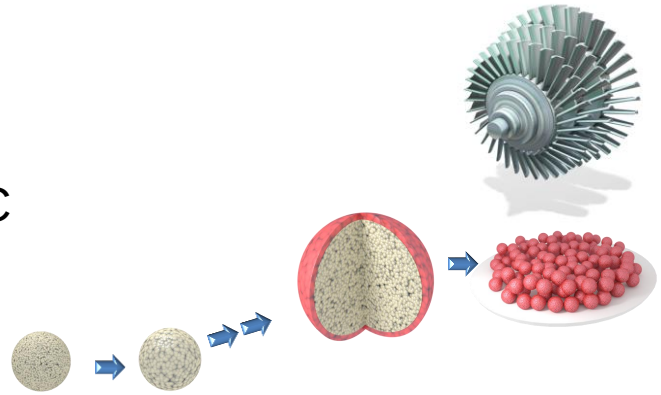
absorbing matrix

- Al_2O_3
- Cr-doped $YAlO_3$
- ...

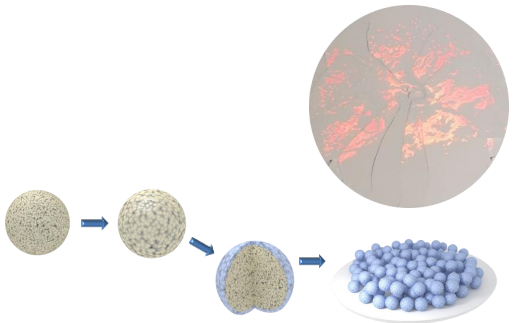


Summary

- **application as TBCs**
  - ➢ synthesis of zirconia microparticles
  - ➢ high-temperature stability by Y-doping up to 1400 °C
  - ➢ encapsulation with Alumina



- **application as structural colors**
  - ➢ synthesis improvement for small ZrO_2 core particles
  - ➢ synthesis improvement for ZrO_2@SiO_2 core-shell particles
    - ✓ monodisperse and single-core particles
    - ✓ high-temperature stability
    - ✓ optical properties of photonic glasses



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