Synthesis and Thermal Stability of Monodisperse ZrO$_2$@SiO$_2$ Core-Shell Submicron Particles

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

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

YSZ / ZrO$_2$ Core Synthesis

YSZ/ZrO$_2$@SiO$_2$ Core-Shell Synthesis

YSZ/ZrO$_2$@Al$_2$O$_3$ Core-Shell Synthesis

TBC

YSZ/ZrO$_2$@SiO$_2$ Photonic Glasses

SC
Outline: Thermal Barrier Coatings (TBC)
Y-Stabilized ZrO₂ Microparticles Show High IR-Reflectivity

Motivation: Thermal Barrier Coatings (TBC)

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

photonic TBCs from ceramic microparticles

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Temperature Stability of ZrO$_2$ Microparticles is Size Dependent

Temperature Stability of ZrO$_2$ Investigated by Scanning Electron Microscopy

t: tetragonal
m: monoclinic

Improved Temperature Stability of Y-Stabilized ZrO$_2$ Microparticles

Temperature Stability of YSZ Investigated by Scanning Electron Microscopy

<table>
<thead>
<tr>
<th>Size</th>
<th>0% Y</th>
<th>4% Y</th>
<th>6% Y</th>
<th>10% Y</th>
<th>16% Y</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2813 nm ± 6.0%</td>
<td>1935 nm ± 17%</td>
<td>2147 nm ± 10%</td>
<td>1875 nm ± 8.7%</td>
<td>2163 nm ± 12%</td>
</tr>
</tbody>
</table>

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

Outline: Structural Colors (SC)

- YSZ / ZrO$_2$ Core Synthesis
- YSZ/ZrO$_2$@SiO$_2$ Core-Shell Synthesis
- SC YSZ/ZrO$_2$@SiO$_2$ Photonic Glasses
Pigmented Colors Selectively Absorb Light, Structural Colors Selectively Reflect Light

Pigmented Color vs. Structural Color

pigmented color

selective absorber

broadband reflector

structural color

core-shell particles (selective reflector)

substrate (broadband absorber)
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.

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

\[
\text{Cd(S}_x\text{Se}_{1-x})
\]

Cr-doped YAlO\textsubscript{3}

Reflection Spectrum dependent on Particle Diameter and Effective Refractive Index

Reflectivity: Fresnel Equation


\[ d \approx \frac{\lambda_e}{2n_{\text{eff}}} \]  
(Fresnel)
Reflection Spectrum dependent on Particle Diameter and Effective Refractive Index

Reflectivity: Fresnel Equation

\[ d \approx \frac{\lambda_e}{2n_{\text{eff}}} \]  

(Fresnel)

Core Synthesis: ZrO$_2$ Submicroparticles

- Hydrolysis
- Polymerisation
- Aggregation

Particle Size Reduction Leads to Rougher Surface and Larger Size Distributions

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

SEM: undoped ZrO₂ particles

\[ d = 421 \text{ nm} \pm 7\% \]

TEM: YSZ particles

\[ d = 123 \text{ nm} \pm 12\% \]
Literature-Known Synthesis of Silica-Shell by using Coupling Agents

Core-Shell Synthesis: ZrO$_2$@SiO$_2$ Particles

ZrO$_2$ with PVP as coupling agent (literature)

PVP: Polyvinylpyrrolidone

ZrO$_2$@SiO$_2$
Encapsulation with Silica by using Self-Adhesive Silica Seeds

Core-Shell Synthesis: ZrO$_2$@SiO$_2$ Particles

ZrO$_2$ with SiO$_2$ seeds on the surface

ZrO$_2$ with PVP as coupling agent (literature)
Stepwise Growth of a Smooth Silica-Shell

Mechanism of Silica-Shell growth

In literature: silica-shell growth on gold nanoparticles

In our synthesis: silica-shell growth on zirconia submicroparticles
Core-Shell Structure Visible in TEM after Focused Ion Beam Lamella Preparation

Characterization: Focused Ion Beam (FIB)

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

Characterization: Scanning Electron Microscopy (SEM)
Improved Temperature Stability of Silica-Encapsulated Zirconia Submicroparticles

Temperature Stability: ZrO$_2$ Particles vs. ZrO$_2$@SiO$_2$ Core-Shell Particles

ZrO$_2$

\[ d_{\text{core}} = 421 \pm 31 \text{ nm (} \sim 7 \% \) \]

ZrO$_2$@SiO$_2$

\[ d_{\text{core-shell}} = 469 \pm 25 \text{ nm (} \sim 5 \% , 76 \text{ nm shell} \) \]
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Temperature Stability: ZrO$_2$ Particles vs. ZrO$_2$@SiO$_2$ Core-Shell Particles

ZrO$_2$ vs. ZrO$_2$@SiO$_2$ at 800 °C
Improved Temperature Stability of Silica-Encapsulated Zirconia Submicroparticles

Temperature Stability: ZrO₂ Particles vs. ZrO₂@SiO₂ Core-Shell Particles
Improved Temperature Stability of Silica-Encapsulated Zirconia Submicroparticles

Temperature Stability: ZrO$_2$ Particles vs. ZrO$_2$@SiO$_2$ Core-Shell Particles

**SEM**

ZrO$_2$

ZrO$_2$@SiO$_2$

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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

\[ d_{\text{core-shell}} = 172 \text{ nm} \pm 9 \% \]

\[ d_{\text{core-shell}} = 272 \text{ nm} \pm 8 \% \]
Sharper Reflection Edge is Needed by Reducing the Core-Shell Size and Dispersity

Optical Properties of ZrO$_2$@SiO$_2$ Photonic Glasses

$d_{cs} = 270$ nm (120 nm core)
$d_{cs} = 450$ nm (360 nm core)
simulation
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:
- $\text{Al}_2\text{O}_3$
- Cr-doped $\text{YAIO}_3$
- ...

Diagram showing light scattering through a structured film with absorption.
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 ZrO₂ core particles
  - synthesis improvement for ZrO₂@SiO₂ core-shell particles
    - monodisperse and single-core particles
    - high-temperature stability
    - optical properties of photonic glasses
Acknowledgements

- Head of Group: Prof. Dr. H. Weller
- Supervisor: Dr. T. Vossmeier
- SFB 986: G. Dahl (C6), K. Furlan (C5), G. Shang (C2), Y. Nguyen (C4), M. Blankenburg (Z2), Prof. Dr. M. Eich (C2), Dr. R. Janßen (C5), Prof. Dr. M. Müller (Z2), Dr. A Petrov (C2)
- Master Thesis: J. Rüter, S. Döring
- Bachelor Thesis: M. Hemme
- Dr. E. W. Leib
- Technical Service: A. Kornowski, R. Schön, S. Werner, A. Barck