Progress in Inorganic-Organic Hybrid Materials by New Precursor Concepts

Ulrich Schubert
Institute of Materials Chemistry
Hybrid Materials: Building Blocks

Inorganic Building Blocks

Connecting Blocks

Organic Building Blocks

Composite

Material 1

Material 2

Hybrid material

Macroscopic phases

Molecular building blocks

Mechanical, optical, electrical, magnetical properties

Reduction of the crosslinking density, coupling sites between inorganic / organic components

Functional groups, crosslinking, polymerizability

Flexibility, elasticity, processability
**Films with Complex Compositions and Polymodal Pore Structure**

**Trimodal pore size distribution:**
- Macropores from polystyrene spheres (100 nm) as porogenes
- Meso- and micropores by removal of surfactant (as porogene) and organic groups

**Complex composition**
- Use of metal alkoxide mixtures
- 1st organic function from R’-Si(OR)₃ precursors
- 2nd organic function by post-synthesis functionalization of the metal oxide structures, e.g. with phosphonic acids
From Building Blocks to Preformed Modules

Shape
Function
Kind of linkage
Connector sites: number and geometrical arrangement

and arrangement “by chance”

and arrangement according to a master plan
From Simple Molecular Building Blocks to Modules

((RO)₃Si)(A)ₙ

Inorganic nano building blocks (NBB)

Spherosilicates or POSS

Bimetallic precursor

Si(OR)₃

Zr₄O₄(methacrylate)₁₂
New Approaches

- New precursor concepts
- Organo-bridged bimetallic precursors
- Pre-formed modules
Coordination Chemistry of Ti(OR)$_4$: Chelating Ligands (CL)

\[ \text{Ti(OR)}_4 + \text{CL-H} \rightarrow \text{Ti(OR)}_3\text{CL} + \text{ROH} \]

Chelating ligands:

X = OR or NHR

R. J. Errington et al., 1998
Organic Modification of Ti(OR)$_4$ by Acetaldoxime

Acid-catalyzed hydrolysis of
- Ti(OiPr)$_4$ + Pluronic F127
- Ti$_2$(OiPr)$_4$(ON=CHMe)$_4$
- Ti$_2$(OiPr)$_4$(ON=CHMe)$_4$ + Pluronic F127

Surfactant for particle stabilization

Calcination temperature

<table>
<thead>
<tr>
<th></th>
<th>250°C</th>
<th>300°C</th>
<th>350°C</th>
<th>400°C</th>
<th>500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) F127 + oxime</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET (m$^2$/g)</td>
<td>151</td>
<td>110</td>
<td><strong>219</strong></td>
<td>197</td>
<td>77</td>
</tr>
<tr>
<td>D$_{BJH}$ (nm)</td>
<td>6.7</td>
<td>10.4</td>
<td><strong>6.7</strong></td>
<td>4.2</td>
<td>14.7</td>
</tr>
<tr>
<td>(b) only oxime</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET (m$^2$/g)</td>
<td>17</td>
<td><strong>154</strong></td>
<td>154</td>
<td>82</td>
<td>39</td>
</tr>
<tr>
<td>D$_{BJH}$ (nm)</td>
<td>13</td>
<td><strong>3.9</strong></td>
<td><strong>4.4</strong></td>
<td>4.1</td>
<td>6.7</td>
</tr>
<tr>
<td>(c) only F127</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET (m$^2$/g)</td>
<td>180</td>
<td><strong>178</strong></td>
<td>147</td>
<td>106</td>
<td>64</td>
</tr>
<tr>
<td>D$_{BJH}$ (nm)</td>
<td>5.4</td>
<td><strong>3.9</strong></td>
<td>4.2</td>
<td>5.6</td>
<td>12.5</td>
</tr>
</tbody>
</table>

calcination at 400 °C for 2h
Ligand-assisted Template Syntheses

\[ \text{SiO}_2 \text{ precursor} \rightarrow \text{Surfactant-coordinated metal alkoxide} \rightarrow \text{self-assembly} \rightarrow \text{template removal} \rightarrow \text{mesostructured metal-doped silica} \]

SiO\(_2\) precursor + \( M(OR)_x \) → \( M - \text{Surfactant Complex} \)

\( M = \text{Ti, Zr, Zr, Hf, Fe, etc} \)

Long-Chain Oximates as Reaction Moderators + Surfactants

\[ \text{Ti(OiPr)}_4 + \text{C}_{11} \text{ oxime} \quad \text{or} \quad \text{Ti(OiPr)}_4 + \text{C}_7 \text{ oxime} \]

\[
\begin{array}{c}
\text{C}_{11} \text{ oxime} \\
\text{C}_7 \text{ oxime}
\end{array}
\]

\[
\begin{array}{c}
\text{after calcination at 350°C}
\end{array}
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S^{BET}[m^2/g])</th>
<th>(D^{BJH}[\text{nm}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_7 \text{ oximate-modified Ti(OiPr)}_4)</td>
<td>175</td>
<td>4.7</td>
</tr>
<tr>
<td>(\text{C}_{11} \text{ oximate-modified Ti(OiPr)}_4)</td>
<td>175</td>
<td>3.3</td>
</tr>
<tr>
<td>(\text{Ti(OiPr)}_4 + \text{Pluronics})</td>
<td>147</td>
<td>4.2</td>
</tr>
<tr>
<td>(\text{Ti(OiPr)}_4 + \text{Brij56})</td>
<td>193</td>
<td>3.3</td>
</tr>
</tbody>
</table>
New Approaches

- New precursor concepts
- Organo-bridged bimetallic precursors
- Pre-formed modules

* Chemical link between two metal alkoxide moieties:
  - to avoid macroscopic phase separation
  - to pre-organize the inorganic structures
Bimetallic Metal Alkoxide Precursors

(Excluding precursors with OR-bridges between the metals)

$$(\text{EtO})_3\text{Si-O-Al(OBu)}_2$$
J. C. Pouxviel et al.

$$(^1\text{BuO})_3\text{SiO-Ti-OSi(O}^1\text{Bu})_3$$
$$\text{OR}^1 \quad \text{OR}^2$$
R$^1$ = R$^2$ = Si(O$^1$Bu)$_3$  T. D. Tilley et al.
R$^1$ = iPr, R$^2$ = iPr or Si(O$^1$Bu)$_3$  Y. Abe et al.

$$\begin{array}{c}
\text{OEt} \\
\text{Ti} \\
\text{OEt} \\
\text{Si(OtBu)_3} \\
\end{array}$$
E. L. Ko et al.

$$(\text{MeO})_3\text{Si-M(OR)}_n$$
M = Al, Ti, Zr, etc.
Gelation of Silica / Titania Systems

Sol-gel processing of Si(OR)$_4$ + Ti(OR)$_4$

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</table>

Gels from

\[
\text{Ti(OR)}_3 (\beta\text{-diketonate})
\]

immediate precipitation of titania gels
(higher reactivity of Ti(OR)$_4$ towards water)
SAXS Studies of Gelation Process

Gelation of \( \text{Si(OR)}_3 \) and \( (\text{RO})_3\text{Si} \)

Scattering feature caused by Ti (characteristic radius \( \approx 0.5 \) nm)

Gel time 150 min

Time evolution of parameter \( A \) (corresponds to primary particle volume \( \Rightarrow r = 0.5 \pm 0.1 \) nm)

Time evolution of parameter \( \xi \) (corresponds to aggregate size)

SAXS: Prof. Herwig Peterlik, Univ. of Vienna
Metal Oxide Nanoparticles in a Silica Matrix I

SiO₂/TiO₂ from

Phase development

Crystallite diameters

Intensity [a. u.]

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Intensity</th>
</tr>
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<tbody>
<tr>
<td>800</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td></td>
</tr>
</tbody>
</table>

* = Anatase
+ = Rutile
o = Cristobalite

*(RO)₃Si

Crystallite Size [Å]

Temperature [°C]

20 30 50 100 150 200 250 300 350

* = Anatase
+ = Rutile
o = Cristobalite
Nanoparticles by Post-Synthesis Treatment of Gels

\[ (RO)_3Si-(CH_2)_n-X-M \]

- **A** ~~~~ **B**
- **Sol-gel processing**
- **Degradation of organic groups**
- **Matrix from the A part of the precursor mixture**

**Coordinating organic group**

**Metal or metal-containing group**
Metallic nanoparticles
Narrow particle size distribution
Variable particle sizes
Variable metal content (up to 50 mol%)
No aggregation of the particles
Homogeneous distribution in the SiO$_2$ matrix
Core-Shell-Particles with Complex Structures

SiO₂ particle with Poly(N-dicarbazolyl-lysine) shell

Si(OEt)₄

H₂O

SiO₂@PDCL@Al₂O₃ composite particles

R’COOH + Zr(OR)₄ → “Zr(OR)₃(OOCR’)” + ROH

Cooperation with J.P. Lellouche, Bar-Ilan University, Israel
Application to Complex Particle Structures

**SiO$_2$@PDCL**

1. Ag$^+$ / AEAPTS
2. Si(OEt)$_4$, H$_2$O
3. $h\nu$

**SiO$_2$@PDCL-ZrO$_2$**

1. Zr(OR)$_4$
2. H$_2$O
3. $h\nu$

**SiO$_2$@PDCL-ZrO$_2$@(Ag@SiO$_2$)**

**AEAPTS =**

\[(RO)_3Si\text{NH}_2\]

Cooperation with J.P. Lellouche, Bar-Ilan University, Israel
New Approaches

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Pre-formed Modules: Clusters with Functional Ligands

Cage compounds as an alternative to network structures
(upon hydrolysis/condensation of metal alkoxides)

Silsesquioxanes ($X = R$)
and Spherosilicates ($X = O^-$)

$\text{Ti}_6\text{O}_4(\text{OEt})_8(\text{methacrylate})_8$
Cluster-Reinforced Organic Polymers

Clusters as pre-formed modules (nanosized building blocks) for the synthesis of class II inorganic-organic hybrid materials

Why clusters?
- Well defined structures
- Deliberate surface modifications
- High interface area
- Clusters are molecules

Why covalent bonds?
- No leaching
- Control of agglomeration
- No migration in the polymer

Polymerizable groups X
Free radical polymerization, ROMP, click reaction, thiol-en polymerization

Initiator groups X
ATRP
Methacrylate-Substituted Metal Oxide Clusters: Examples

OMc = methacrylate
Carboxylate-Substituted Metal Oxide Clusters
Variation of the Functional Organic Groups

Fee radical polymerization
⇒ X = acrylate, methacrylate, styryl groups etc.

Ring-opening metathesis polymerization (ROMP)
⇒ X = norbornenyl groups

Click reaction
⇒ X = alkinyl-substituted groups

Atom-transfer radical polymerization (ATRP)
⇒ X = halogenated groups, (e.g. OOC-CBrMe₂)

G. Kickelbick

Thiol-ene reaction
⇒ X = SH-containing groups, (e.g. OOC-CH₂CH₂SH)

S. Gross

Zr₆O₄(OH)₄(methacrylate)₁₂

Zr₆O₄(OH)₄(5-norbornene-2-carboxylate)₁₂

Ti₆O₄(OPr)₈(OOC-CH₂CH₂C≡CH)₈

Ti₆O₄(OPr)₈(OOCCBrMe₂)₈

[Hf₆O₄(OH)₄(OOC-CH₂CH₂SH)₁₂]₂
The properties of the cluster*-based hybrid materials originate from the high crosslinking efficiency in combination with "nanofiller" effects. The properties not only depend on the polymerization conditions and the cluster proportion, but also on the kind of employed cluster.

- Increased thermal stability
- Adjustable swelling in organic solvents
- Improvement of thermomechanical properties and tensile strength
- Modification of dielectric properties
- Incorporation of clusters with special intrinsic properties, e.g. superparamagnetic clusters

* Oxo clusters of Ti, Zr, Hf, Ta, Mn
Dispersion of \( \text{Mn}_{12}\text{O}_{12}(\text{acrylate})_{16} \) in Poly(ethylacrylate)

\[
\text{Mn}_{12}\text{O}_{12}(\text{OOC-CH}_3)_{16} + \text{CH}_2=\text{CH-COOH} \rightarrow \text{Mn}_{12}\text{O}_{12}(\text{OOC-CH=CH}_2)_{16} - \text{CH}_3\text{COOH}
\]

Radical polymerization

\[+ \text{CH}_2=\text{CMe-COOEt}\]

(Superparamagnetic) PMMA crosslinked by \( \text{Mn}_{12} \)

"\( \text{Mn}_{12} \)" : total cluster spin \( S = 10 \) (4 Mn\text{IV}, \( S = \frac{3}{2} \) + 8 Mn\text{III}, \( S = 2 \))

SAXS:

One characteristic length

Cluster-cluster distance changes from 1.6 to 3.2 nm when cluster proportion is decreased

0.5 mol\% cluster

4 mol\% cluster
Acknowledgements

Money

Fonds zur Förderung der wissenschaftlichen Forschung