La sintesi chimica dei materiali porosi nanostrutturati e le applicazioni in catalisi e nella sensoristica

Parte 2: applicazioni

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Multi-component inorganic oxides
Sol-gel Method

- Hybrid O/I films
- SiOC/ZrO$_2$  SiOC/TiO$_2$
- SiO$_2$/SnO$_2$
- ZrO$_2$  TiO$_2$  V$_2$O$_5$
- TiO$_2$/V$_2$O$_5$  NiO/V$_2$O$_5$  Bi$_2$O$_3$/V$_2$O$_5$
- BaO/TiO$_2$  BaTiO$_3$
Hybrid Sol-Gel materials

- Multicomponent materials prepared at low temperature by sol-gel chemistry
- Alkoxide precursors modified with organic groups
- Presence of organic groups in the inorganic network
  (Si-C bond stability towards hydrolysis)

Obtained materials display chemical and surface properties that are intermediate between inorganic networks and organic polymers

Hybrid materials:
Class I: Van der Waals interactions between organic and inorganic parts
Class II: covalent bonds between the two counterparts
Hybrid O/I films as chemical sensors

Hybrid O/I films used as sensing elements:

- Porosity, chemical properties of the film surface can be tuned
- Films can operate at ambient temperature
- Detection of alcohols (vapours) from their electrical responses
- Detection of aromatic and alkane vapours from their optical properties
- Detection of aromatic molecules from their changes in UV-absorption spectra (molecule and molecule + film)

Why aromatic molecules?

<table>
<thead>
<tr>
<th>Molecule</th>
<th>TWA [ppm]</th>
<th>STEL [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Toluene</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>O-Xilene</td>
<td>100</td>
<td>150</td>
</tr>
</tbody>
</table>

Directive 2000/69/EC: TLV for benzene in air: \textbf{1.6 ppb} (starting from 2010)

High sensitivity sensors

TWA = Time Weighted Average
STEL = Short Term Exposure Limit
Synthesis of hybrid films

- TEOS, EtOH, H₂O
  - EtOH/Si = 4/1
  - H₂O/Si = 1/1
  - pH = 2, 7
- Pre-hydrolysis, 1h
- MTES or GLYMO addition
- Stirring, 0.5 h
  - TM 7/3 and 9/1
  - TG 7/3 and 9/1
- Dip-coating
  - r = 6 cm/min

- • film thickness: ~ 1µm
- • film area: ~ 4 cm²
Film characterization

XRD spectra

- Intense peak attributable to silica network (analogous to mesoporous SiO$_2$)
- Second peak (>d) due to the O/I phase interaction?
- TM 7/3 film: different situation: shift to lower d values and decrease of “inorganic” peak intensity
- TM and TG 7/3 films: presence of a halo (~ 6°) due to the higher network modifier content (M pure gel)
Instrumental set-up

Sampling chamber

Line 1: Carrier gas

Line 2: Carrier gas + molecule

Flowmeters

Sampling chamber: $V = 1 \text{ dm}^3$

Aromatic molecule (liquid) in a bubbler (vapor pressure)
Results: absorbance spectra

- Film interaction: decrease in absorbance of the molecule
- No peak broadening or fine structure vanishing: surface interaction and no diffusion into the film
- Spectral features of the molecule remains: different $\lambda$ values of Max absorbance: qualitative analysis
Results: reversibility of the interaction

For all film compositions and for all molecules, nitrogen purging allows the complete recovering of the film trapping features (Max. 20 min)
Results: comparison of film performances

With the same experimental conditions, different film/molecule interactions → different selectivities
Benzene: weak interactions with film surface
O-Xilene: strong interactions with all films
Parametric refinement of kinetic curves

• In order to characterise different adsorption film capabilities, a simple model has been assumed for the kinetic behavior.
• When the measurement chamber is empty, the filling rate can be determined as:

\[ n(t) = n_0 \cdot \left(1 - e^{-t/\tau_0}\right) \]

\( \tau_0 \) (sec) is related to the chamber filling time.

• When the film is inserted into the chamber, the whole adsorption process can be expressed as:

\[ n(t) = A_1 \cdot \left(1 - e^{-t/\tau_0}\right) + A_2 \cdot \left(1 - e^{-t/\tau_a}\right) \]

\( \tau_a \) (sec) is related to the adsorption onto the film surface.

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Results: fitting of data

\[
y = 0.48061 \left(1 - e^{-x/81.9672}\right) + 0.05858 \left(1 - e^{-x/397.87}\right)
\]

Statistical parameters:
\[\chi^2 = 0.00003\]
\[R^2 = 0.99726\]

<table>
<thead>
<tr>
<th>(\tau_a) values for benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM 9/1</td>
</tr>
<tr>
<td>TG 9/1</td>
</tr>
<tr>
<td>TM 7/3</td>
</tr>
<tr>
<td>TG 7/3</td>
</tr>
</tbody>
</table>
Results: adsorption of benzene

- Benzene steric hindrance: 6Å
- Adsorption on the film surface (micropores)
- Reversibility of the interaction
- $\tau_a$ values that depend on electronic effects:
- TM 9/1 and TG 9/1: higher degree of interaction between Si-OH / $\pi$ electrons of benzene (hydrogen bond) → high $\tau_a$ values
- TG 7/3 and TM 7/3: higher content of “organic” groups on the pore surface → weaker interaction with $\pi$ electrons → low $\tau_a$ values
Hybrid O/I films for wine characterization

Cyclic Voltammetry (CV)

Working electrode: O/I film
Counter electrode: Pt
Reference electrode: Ag/AgCl
Hybrid O/I films for wine characterization

White and red wines are well separated

TA films show different behaviour: presence of $\text{–NH}_2$ groups that are protonated in acidic solutions
Thermal evolution of SiOC phase in the presence of the metal oxide

Metal load influences Si-C bond stability

Different structural evolution of polysiloxane - titania gels as a function of metal load
Synthesis of xerogels

**Pre-hydrolysis**
H₂O, HCl, EtOH

**Preceramic Polymers**

**Ceramization Process**

**Gelation**

Me, x mol%

DMex

**Thermal treatments (Ar)**

- 500 °C
- 800 °C
- 1000 °C
- 1600 °C

**Characterization of samples**

- IR
- TGA
- N₂-sorption
- XRD
**Thermal evolution and porosity**

**Thermal analysis**

- **DTi10**: two weight losses
- **DTi30**: one weight loss
- **DTi30** thermal evolution is completed at 600 °C, **DTi10** above 800 °C

**N₂-Sorption**

- **DTi30**: maximum SSA value at 500 °C (175 m²/g)
- **DTi10**: maximum SSA value at 800 °C (384 m²/g),
  - high SSA values up to 1000 °C (273 m²/g)
Ceramization process

Increase of the metal oxide load:

1. decreases the stability of polysiloxane-oxide network (due to the increase in phase interaction) ⇒
   ⇒ Si-C bond cleavage (low temperature)

2. Evolution of methane and Si-based species at low temperatures

3. Favours the polymer-to-ceramic conversion
Phase evolution

**Amorphous phases**

- \( \text{SiC}_x \text{O}_{2(1-x)} \) phase (SiOC): stable up to 1600 °C (except DTi30)
- \( \text{TiO}_x \text{C}_{1-x} \) phase (TiOC): 800 °C (all DTix)

**Evolution**

\[ \text{SiC}_x \text{O}_{2(1-x)} \rightarrow \text{SiO}_2 \ (\text{+ SiC for DTi10}) \]

**Crystalline phases**

- \( \text{TiO}_2 \): 1000 °C (all DTix)
- \( \text{TiO}_x \text{C}_{1-x} \rightarrow \text{TiC} \ (\text{+ Ti oxides (DTi20 and DTi30)}) \)
- \( \text{SiO}_2 \) cristobalite (DTi30 at 1400 and 1600 °C)
SiOC phase evolution

When the carbon content retained into the phase is higher, the phase density is higher and its a parameter value is lower.

Increasing Ti %: lower C content and higher a value.

All DTix: final amorphous phase is pure SiO$_2$ (loss of C).

DTi30: crystallization of cristobalite (tetragonal) starts at 1400 °C.
SiO$_2$/SnO$_2$ Systems

Homogeneous dispersions of M(IV)-oxide particles in silica matrix

Applications: catalysts, sensors, optical fibers

Requirements: control on the
- thermal stability
- particle sizes
- porosity
- development of suitable phases
Sol-Gel Synthesis

\[ \text{Si(OEt)}_4 \quad \text{H}_2\text{O} \quad \text{pH} = 2 \quad \text{Sn(OEt)}_4 \text{ in THF} \]

\[ [\text{Si(OEt)}_4] = 1\text{M} \quad \text{Molar ratio:} \quad \frac{\text{H}_2\text{O}}{\text{Si}} = 2 \]

\[ [\text{SnO}_2] = 0.13 \text{g/ml} \]

Sol preparation \( \approx 3 \text{ days} \)

Gelification

Monolithic gels
(dimensions decrease with tin content)

Samples
\[ \text{SiO}_2/\text{SnO}_2: \]
(weight ratios)
\[ 95/5 \quad 90/10 \quad 80/20 \quad 70/30 \]

Thermal treatments
(Air, O\(_2\), He)

Characterization techniques:
DTA, N\(_2\)-physisorption, IR, XRD,
Mössbauer spectroscopy
Increasing Sn content:
• increase of -OH groups (≈ 3400, 1650 cm\(^{-1}\))
• increase of Si-OH + Si-O-Sn bands (950 cm\(^{-1}\))
• increase and broadening of Sn-O band (≈ 650 cm\(^{-1}\))

Increase of the structural disorder of tin species
Temperature Effect

Crystallization behaviour:
SiO$_2$/SnO$_2$ 70/30 samples treated in air
XRD spectra

- Increasing Sn content, crystallization of SnO$_2$ occurs at lower temperature, where the matrix is still amorphous (primary crystallization)

- For 95/5 sample, crystallization occurs at 1160 °C (decomposition of the matrix in SiO$_2$ + SnO$_2$)
Temperature Effect

Crystallization behaviour:
SiO₂/SnO₂ samples treated in air
DTA curves

Primary crystallization temperature increases when tin content lowers
Phase evolution by the heat treatment

XRD spectra of samples heated at 1400 °C

Oxygen
Air
Helium

- Tin content and the heat treatment stabilize different silica polymorphs
- Low tin content and inert atmosphere support the reduction to metal tin by the decomposition of Sn(II): $2\text{SnO} \rightarrow \text{Sn} + \text{SnO}_2$
Synthesis of Y-ZrO$_2$ porous films

Zr(OPr)$_4$ (70% solution in PrOH) -> Hydrolysis with water excess (molar ratio: Zr(OPr)$_4$/H$_2$O = 1/160)

30 min. at R.T. -> ZrO$_2$ x H$_2$O

3-4 days at 90°C -> Peptization with HCl (12.5 M; molar ratio: Zr(OPr)$_4$/HCl = 1/1.43)

ZrO$_2$ sol

Organic compound (organic/Σ metal oxides = 20 wt% / 80 wt%) -> 1 h at R.T.

Y(OAc)$_3$.4 H$_2$O (90 mol% ZrO$_2$ / 10 mol% Y$_2$O$_3$) -> 1 h at R.T.

Casting on PP, drying, xerogels within several days at R.T.

Organic compound:
- PVA
- dextran
- sucrose
- starch
- albumin
- CMC
Synthesis of Y-ZrO$_2$ porous films

SURFACE AREA AND MICROPOROE AREA BY N$_2$ SORPTION ANALYSIS

(1200°C, air, 5°C/min, 1 h isotherm)

<table>
<thead>
<tr>
<th>Organic compound</th>
<th>Surface area ± SEM$^a$ (m$^2$/g)$^b$</th>
<th>Micropore area (m$^2$/g)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>10.08 ± 0.11</td>
<td>1.93</td>
</tr>
<tr>
<td>dextran</td>
<td>6.55 ± 0.23</td>
<td>3.11</td>
</tr>
<tr>
<td>sucrose</td>
<td>4.38 ± 0.20</td>
<td>1.59</td>
</tr>
<tr>
<td>starch</td>
<td>3.68 ± 0.046</td>
<td>1.29</td>
</tr>
<tr>
<td>albumin</td>
<td>3.66 ± 0.047</td>
<td>1.42</td>
</tr>
<tr>
<td>CMC</td>
<td>3.04 ± 0.11</td>
<td>1.29</td>
</tr>
</tbody>
</table>

$^a$ SEM: standard error of mean
$^b$ obtained from BET equation
$^c$ obtained from t-plot
Synthesis of TiO$_2$ nanopowders

Reverse micelles method

Water-in-oil droplets
Formation of a “water pool” → $w = [\text{H}_2\text{O}]/[\text{S}]$

$S = \text{surfactant agent}$

“Reverse micelles”: $w < 15$; “Microemulsion”: $w > 15$

Assumption: spherical droplets
Sphere radius:

$$R_w = \frac{3V_{\text{aq}}[\text{H}_2\text{O}]}{\sigma[S]}$$

$V_{\text{aq}} = \text{Volume of water molecules}$

$\sigma = \text{head polar group area}$
Synthesis of TiO_2 nanopowders

Surfactant:

TRITON X-100 = polyoxyethylene(10) isoctylphenylether

\[ 4-(C_8H_{17})C_6H_4(OCH_2CH_2)_nOH \]
\[ n \sim 10 \]

Molar ratios:

H_2O/alkoxides = 10/1
H_2O/surfactant = 10/1

Materials:

- Ti(OPr')_4 + Cyclohexane
- TRITON X-100 + Cyclohexane

Steps:

- Powder formation
- Reverse micelles
- Filtration
- Drying (T=80°C)
- Film Formation

Time:

- 15 min stirr
- 30 min stirr
- 3-4 times
- 30 min stirr
- 3-4 times
Powder characterization

\( \text{N}_2 \)-physisorption

Type IV-a isotherm \( \rightarrow \) mesoporous system

Specific Surface Area: 170 m\(^2\)/g
Powder characterization

As prepared powder

400 °C-treated powder on glass

Quantitative analysis: 75 % anatase
25 % brookite
S\textsubscript{(adsorbito)} + h\nu \rightarrow S^\circ \textsubscript{(adsorbito)}
S^\circ \textsubscript{(adsorbito)} \rightarrow S^+ \textsubscript{(adsorbito)} + e^- \textsubscript{(iniettato)}
S^+ \textsubscript{(adsorbito)} + 3/2 I^- \rightarrow 1/2 I_3^- + S \textsubscript{(adsorbito)}
I_3^- \textsubscript{(catodo)} + 2e^- \rightarrow 3I^- \textsubscript{(catodo)}

S^\circ \textsubscript{(adsorbito)} \rightarrow S \textsubscript{(adsorbito)}
S^+ \textsubscript{(adsorbito)} + e^- \textsubscript{(TiO2)} \rightarrow S \textsubscript{(adsorbito)}
I_3^- \textsubscript{(anodo)} + 2e^- \textsubscript{(TiO2)} \rightarrow 3I^- \textsubscript{(anodo)}
DSSC preparation

Experimental measurements
Results

Indoor measurements

Outdoor measurements
Synthesis of $V_2O_5$ thin films

Sol-gel method: hydrolysis of vanadium alkoxides

a) $\text{VO(OPr}^i\text{)}_3 + \text{i-PrOH} \rightarrow \text{film deposition (in ambient air)}$

b) $\text{VO(OPr}^i\text{)}_3 + \text{CH}_3\text{COOH} + \text{i-PrOH} + \text{H}_2\text{O} \rightarrow \text{film deposition}$

Hydrolysis: water with pH = 0, 1, 2

c) As b) + (Ti, Zr) alkoxides or (Bi, In, Sb) chlorides

(mixed compositions) $\rightarrow$ film deposition

a), b), c) $\rightarrow$ gels
V$_2$O$_5$ gels and films

Alkoxide-derived gels and films = amorphous

- Microstructural order in films depends on the synthesis conditions (pH of water added during hydrolysis)
- Gels do not show significant changes in unit cell parameters
Thermal analysis of $V_2O_5$ gels

- different thermal behaviour, depending on synthesis conditions
- presence of two exothermal effects
- crystallization of a metastable $V_2O_5$-nanotubes (280-310°C)

**DTA curves**

**Raman Spectra**

(pH = 2 sample)
Electrochromic devices

Simultaneous ionic and electronic conductivities

Inorganic oxides:

WO$_3$ + $x$M$^+$ + xe$^-$ $\rightarrow$ M$_x$WO$_3$ (cathodic)
(clear) (blue)

Fe$^{II}$[Fe$^{II}$(CN)$_6$]$^{13-}$ $\rightarrow$ Fe$^{III}$[Fe$^{II}$(CN)$_6$]$^{12-}$ + e$^-$ (anodic)

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Electrochemical features of $V_2O_5$ thin films

Insertion process: $xLi^+ + V_2O_5 \rightarrow Li_xV_2O_5 \quad x \leq 1$

Gels: $V_2O_5 \cdot nH_2O \quad \Rightarrow \quad \text{Layered structure (2D)}$

- Good cycling reversibility
- High insertion levels of Li$^+$
- Simultaneous reduction
  $V^{5+} \rightarrow V^{4+}$

Residual coloration (both anodic and cathodic)

Use of a “bleaching oxide”

($TiO_2, NiO, In_2O_3, Sb_2O_3, Bi_2O_3, ZrO_2$)
Ti/V oxide systems

Electrochemical behaviour of films

Surfactant effect

Ti/V 1/1 No hydrolysis

Ti/V 1/1 + Triton

Ti/V 1/1 + Brij

Triton: higher stability, more amorphous system

Brij: lower stability
TI/V oxide systems

Film transparency

TI/V 1/10 400 °C

First run
Intercalation
Deintercalation

% Transmittance vs Wavelength (nm)
Electro-optical response in NLC-cells

Typical LC cell configuration

Ti/V 1/1 films

Rectified electro-optical response
**Electrochemical behavior of Ni/V 1/10 films**

**Sol-gel films heated at 400 °C**

**Ni(acac)$_2$**
(70 nm)

**NiCl$_2$**
(60 nm)

- Low charge capacity ($\approx 10 \text{ mC/cm}^2$)
- Oxidation peak and reduction peaks are unchanged

- Low charge capacity ($\approx 10 \text{ mC/cm}^2$)
- Oxidation peak decreases (new shoulder at 1.9 V)
- Reduction peaks tend to vanish
Transmittance spectrum of Ni/V 1/10 film

Sol-gel film from Ni(acac)$_2$ pH = 1

- Transmittance > 80 % in all visible region
- No irreversible changes during cycles
Bi/V 1/10 systems

400 °C treated films

Low charge capacity

Similar results than Ti/V systems
Barium Titanate

Ferroelectric Perovskite $\text{ABO}_3$ class:
Cubic structure
$A =$ mono- or divalent ion (green)
$B =$ tri- to hexavalent ion (grey)

Ferroelectricity strongly related to the crystallite size

Size effect: ferroelectric ceramic lose ferroelectricity at a critical size

$\text{BaTiO}_3$: high-dielectric constant material
Nanocrystalline powders: Multilayer ceramic capacitors (MLCC)
(Piezoelectricity)
nano-sized powders: amorphous $\rightarrow$ low dielectric performance
crystalline $\rightarrow$ ultra thin dielectric layers
Barium Titanate

Polymorphic transformation: Tetragonal $\rightarrow$ Cubic

$T_C = 120 ^\circ C$

$T_C = 75 ^\circ C$ for 120 nm particle size

Grain-size dependent transformation at R.T (tetragonal $\rightarrow$ orthorhombic)

Fig. 8.16. The dependence of the lattice constant ratio of tetragonal $\text{BaTiO}_3$ on the average particle size. [G. Arlt, D. Hennings, and G. de With, J. Appl. Phys. 58, 1619 (1985).]
Synthesis and characterization of BaTiO$_3$ nano-powders

Electrical properties that depend on particle size

Effect of synthesis procedure on particle size and phase evolution

BaTiO$_3$ ⇒ perovskite (cubic) structure ⇒ piezoelectricity

\[
\begin{align*}
\text{CH}_3\text{COOH} & \quad \text{2-PrOH} \\
\text{Mixing} & \quad \text{Ti(OPr$^i$)$_4$} \\
\text{Hydrolysis} & \quad \text{H}_2\text{O} \\
\text{Gelation} & \quad 80 \, ^\circ\text{C} \\
\text{Powder} & \quad \text{Ba(CH}_3\text{COO)}_2
\end{align*}
\]
Sol-Gel synthesis of BaTiO$_3$

1. Barium acetate / Titanium isopropoxide → hydrolysis
2. Barium isopropoxide / Titanium isopropoxide → hydrolysis
3. Addition of acetic acid as a chelating agent
4. Addition of 2-propanol and ethylene glycol (co-solvent)
5. Refluxing of the reagent solutions

Results

Phase separation: BaCO$_3$ formation during precipitation
No stoichiometric control of the reaction
TiO$_2$ crystallization (excess of Ti)
Thermal treatment: Transformation to tetragonal BaTiO$_3$
phase above 800 °C
No pure BaTiO$_3$ phase
Synthesis of BaTiO$_3$ powders from RM method

Alkoxide precursors

- **Ba(OPr')$_2$**
- Ti(OPr')$_4$
- Cyclohexane

- TRITON X-100
- Cyclohexane

Powder formation

Reverse micelles

Filtration

Drying ($T = 80 \, ^\circ C$)

Thermal Treatment

- TRITON X-100 = polyoxyethylene(10) iso-octylphenylether
- $4-(C_9H_{17})C_6H_4(OCH_2CH_2)_nOH$
- $n \approx 10$

- $H_2O/alkoxides = 10/1$
- $H_2O/surfactant = 2/1$
Synthesis of BaTiO$_3$ powders

Acetate/alkoxide precursors

- Ti(OPr$^t$)$_4$ + Cyclohexane
- TRITON X-100 + Cyclohexane
- BaAc$_2$ + Water

- Powder formation
- Reverse micelles
- Filtration
- Drying ($T = 80 ^\circ C$)
- Thermal Treatment

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Powder characterization
As-precipitated powders
(pure alkoxide route)

Acicular-shaped aggregates
(tetragonal phase)

\( N_2 \)-physisorption analysis
- Type IV-a isotherm
- S.S.A. = 200 m\(^2\)/g
Powder characterization

As-precipitated powders
(pure alkoxide route)

Better control of the stoichiometry (only a slight excess of Ti)

Crystallite size at 1050 °C: ~ 40 nm (BaTiO₃)
**Powder characterization**

As-precipitated powders (acetate/alkoxide route)

450 °C

Static air

No BaCO₃ formation

700 °C

TiO₂ separation

Final products:
- c-BaTiO₃
- BaTi₂O₅
- BaTi₄O₉

Sintesi chimica di materiali porosi nanostrutturati e applicazioni in catalisi e sensoristica