Stazione Sperimentale per la Seta

Textile Research Centre

*Nano*structured photoactive SiO_2-TiO_2 materials for the surface modification of a polyester fabric

F. Rusconi

Stazione Sperimentale per la Seta

Como - Italy

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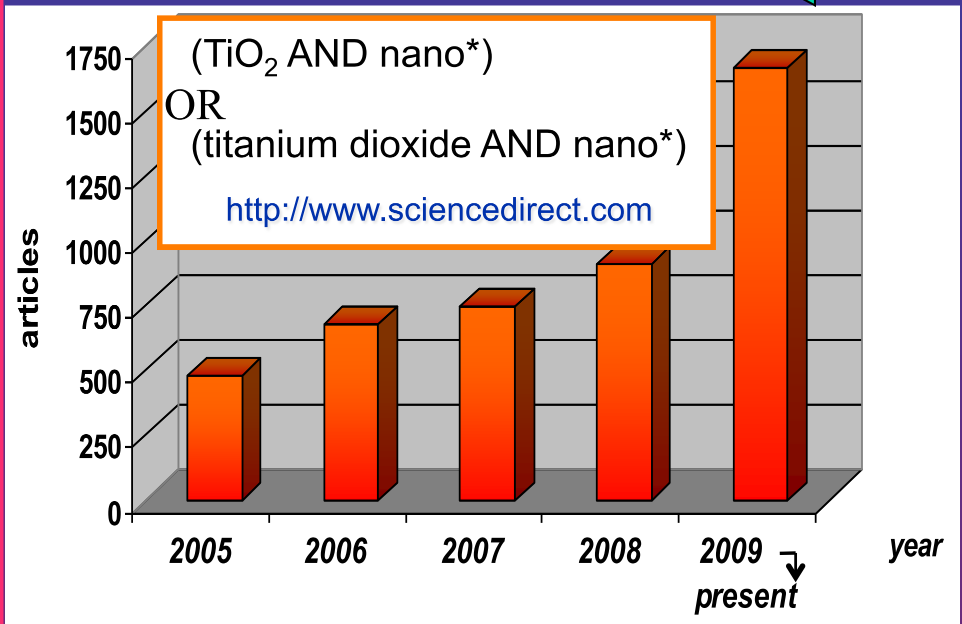
1. INTRODUCTION

Photochemical processes catalyzed
by semiconducting oxides

TiO_2 + composite materials

thin films or powders

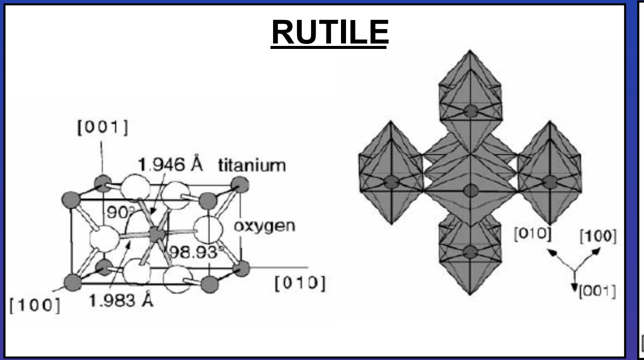
Scientific impact ⇄ Technological applications

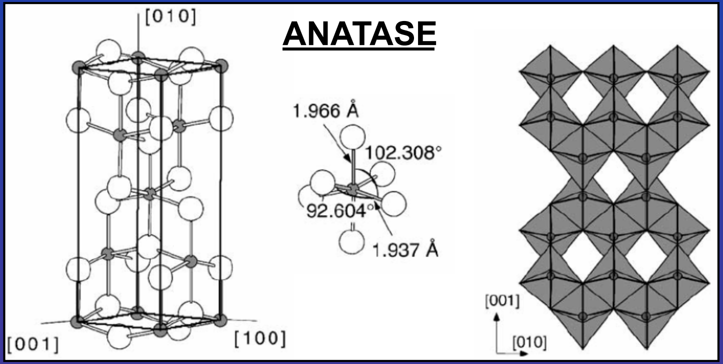


- Air depollution
- Water treatment
- Photovoltaic and solar cells
- Electrical devices
- UV-protection

1.1. INTRODUCTION: TiO_2

- semiconducting material
- high chemical and thermal stability
- commercially available (polycrystalline material)
- easy to prepare



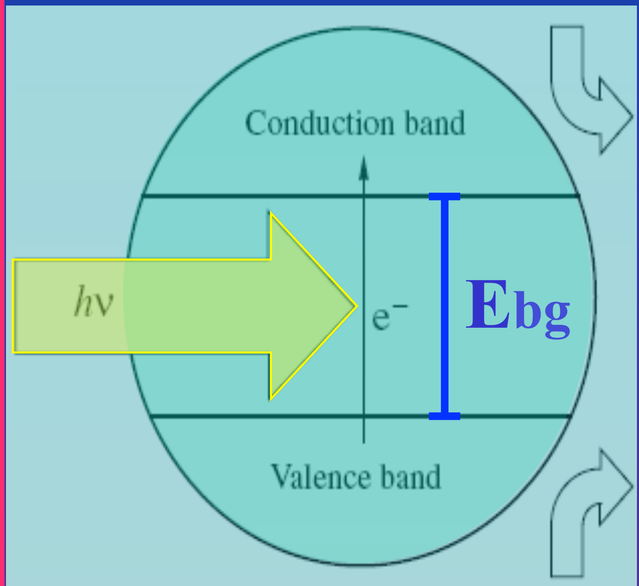


Physico-chemical property:	<u>RUTILE</u>	<u>ANATASE</u>
REFRACTIVE INDEX	2.76	2.52
DENSITY (g/cm^3)	4.25	3.89
$E_{band-gap}$	**3.0 eV → 413 nm**	**3.2 eV → 388 nm**

Titanium dioxide as functional agent coated on the textile surface

1.1. INTRODUCTION: TiO_2

$$TiO_2 + h\nu \xrightarrow{\text{photoexcitation}} TiO_2\,(h^+_{vb} + e^-_{cb})$$



$$TiO_2\,(e^-_{cb}) + O_2 \longrightarrow TiO_2 + O_2^{\bullet -}$$

$$O_2^{\bullet -} + H^+ \longrightarrow {}^{\bullet}HO_2$$

$$2\,{}^{\bullet}HO_2 \longrightarrow O_2 + H_2O_2$$

$$TiO_2\,(h^+_{vb}) + H_2O \longrightarrow TiO_2 + H^+ + {}^{\bullet}OH$$

$$TiO_2\,(h^+_{vb}) + OH^- \longrightarrow TiO_2 + {}^{\bullet}OH$$

$$TiO_2\,(h^+_{vb}) + R\text{-}X \longrightarrow TiO_2 + R\text{-}X^{\bullet +}$$

Very reactive hydroxyl radicals able to degrade inorganic and organic substrates.

Titanium dioxide photocatalysis

1.2. INTRODUCTION: TiO_2 coating

Titanium dioxide photocatalysis

nano-photocatalysts prepared by immobilization of TiO_2-based functional coating on fabrics

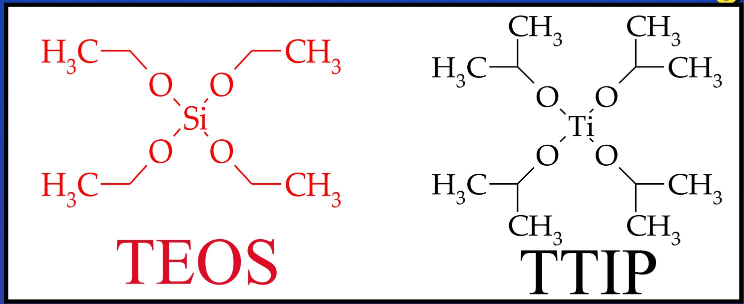
Impart to the textile a series of properties:

1) Air pollution Control
2) Odor abatement
1) Self-Cleaning
2) UV-Protection

Photocatalytic Activity

1.2. INTRODUCTION: SiO_2-TiO_2 coating

Preparation method
of silica-titania materials + coatings



Sol-Gel

Silica is able to afford a 3D network with [1],[2],[3]
- high surface area, likely hosting the anatase nanocrystals,
- high UV-light trasmittance, granting photoactivation of titania,
- stability, being immune to the photo-oxidative action of TiO_2.

SiO_2 is the ideal matrix for titania

We investigated the influence of:
1) systematic variations of the synthetic process,
2) Si/Ti molar ratio,
3) process temperature

on
- **structural properties**
- **<u>photoactivity</u> of xerogels and of the <u>coated textiles</u>.**

[1] *J. Sol Gel Sci. Technol.*, 2000, 19, 585.
[2] *J. Am. Ceram. Soc.*, 2000, 83, 1, 229.
[3] *J. Mol. Catal. A: Chemical*, 2006, 244, 160.

2. Experimental Part

2.1. Preparation of Sols → Xerogels

Route A

SiO_2 sol and TiO_2 sol prepared under acidic conditions,
TEOS/H_2O/EtOH molar ratio = 1:25:15
TTIP/H_2O/EtOH molar ratio = 1:25:15
the 2 sols were then mixed to obtain different Si/Ti:

Route A		
Mixed sol composition (v/v)	**Ageing**	**XEROGEL Label**
Sol_{TEOS} : Sol_{TTIP} 80 : 20	HWT (2h)	**A.1.1**
	80°C (24h)	**A.1.2**
	45°C (24h)	**A.1.3**
	25°C (24h)	**A.1.4**
Sol_{TEOS} : Sol_{TTIP} 65 : 35	HWT (24h)	**A.2.1**
	80°C (24h)	**A.2.2**
	45°C (24h)	**A.2.3**
	25°C (24h)	**A.2.4**
Sol_{TEOS} : Sol_{TTIP} 50 : 50	HWT (24h)	**A.3.1**
	80°C (24h)	**A.3.2**
	45°C (24h)	**A.3.3**
	25°C (24h)	**A.3.4**

Route B

Three sols produced *via* hydrolysis and co-condensation of TTIP + TEOS in the same reactor:
(TEOS+TTIP)/H_2O/EtOH molar ratio was 1:25:15

Route B		
Mixed sol composition (v/v)	**Ageing**	**XEROGEL Label**
TEOS : TTIP 80 : 20	HWT (2h)	**B.1.1**
	80°C (24h)	**B.1.2**
	45°C (24h)	**B.1.3**
	25°C (24h)	**B.1.4**
TEOS : TTIP 65 : 35	HWT (24h)	**B.2.1**
	80°C (24h)	**B.2.2**
	45°C (24h)	**B.2.3**
	25°C (24h)	**B.2.4**
TEOS : TTIP 50 : 50	HWT (24h)	**B.3.1**
	80°C (24h)	**B.3.2**
	45°C (24h)	**B.3.3**
	25°C (24h)	**B.3.4**

Second columns show the ageing conditions to obtain the corresponding xerogels.
Finally they were dried at the ageing temperature; in the case of HWT the drying temperature is 80°C
The obtained xerogels are labelled as in the third column of Tables.

2.2. Xerogels characterization

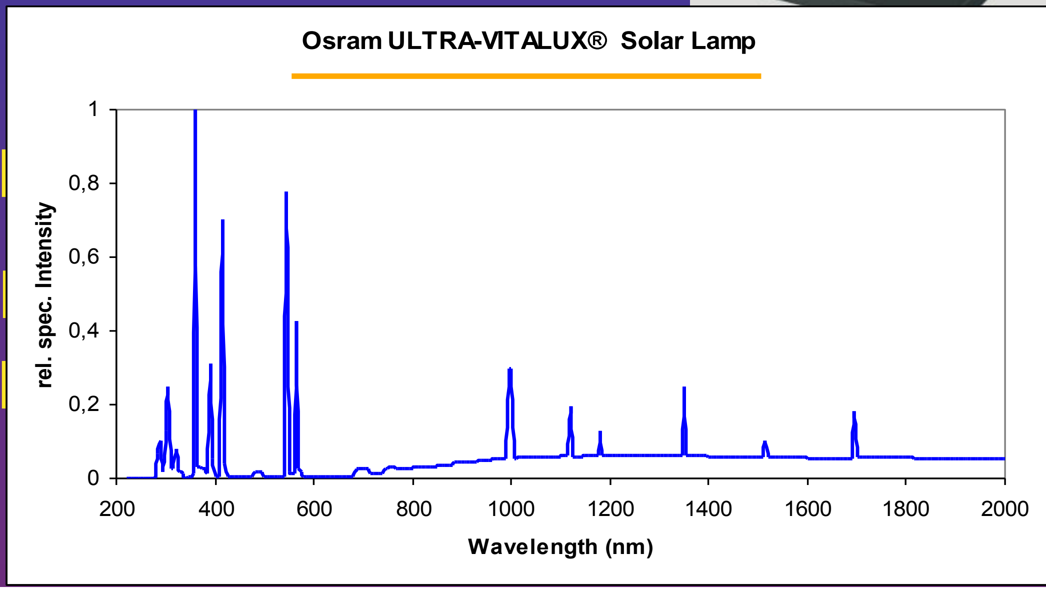
After grinding the xerogels, the corrisponding powders were characterized by:

XRPD → crystalline phase
→ av. size of crystallites (Bruker AXS TOPAS-R software)

microstructure ← N_2-adsorption
← BET surface area
← Pore size
← Pore distribution

Photoactivity →
→

Osram Ultravitalux® Solar Lamp



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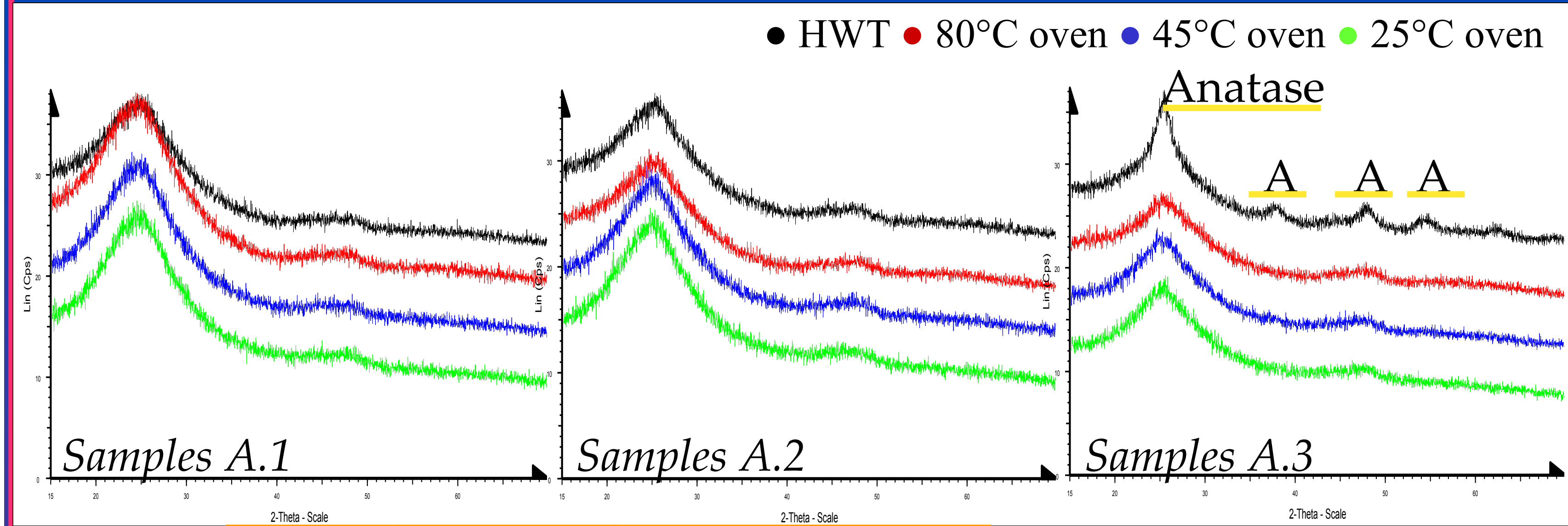
XRPD: samples using Route A



Sample	Crystalline phase	Average Size of crystallites (Ø, nm)
A.1.1	anatase	1,5 HWT
A.1.2	anatase	1,0
A.1.3	anatase	1,0
A.1.4	anatase	1,0
A.2.1	anatase	2,0 HWT
A.2.2	anatase	2,0
A.2.3	anatase	1,5
A.2.4	anatase	1,5
A.3.1	anatase	4,0 HWT
A.3.2	anatase	2,5
A.3.3	anatase	2,0
A.3.4	anatase	2,0

Ti conc.

T

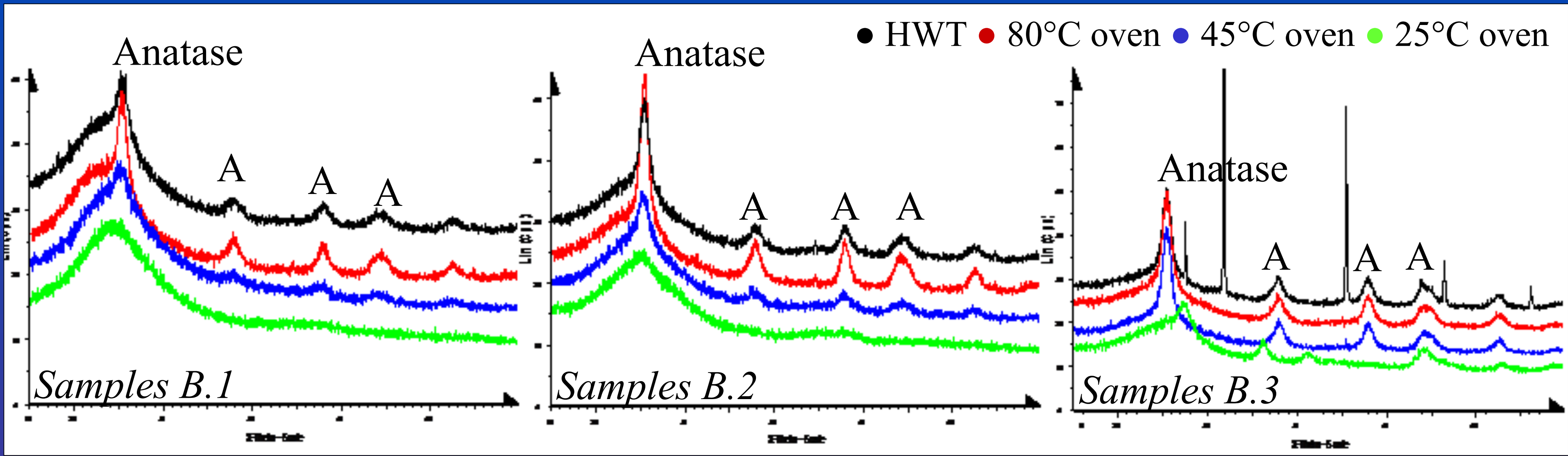
- samples A.1 and A.2: very broad contribution of titania, above a continuous background supplied by the silica matrix :

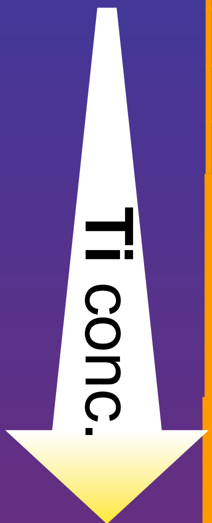
↓

Crystal sizes (Ø) < 2 nm

- sample A.3.1 containing the larger Ti concentration, the pattern clearly shows **Anatase** and Ø = 4 nm is calculated.

XRPD: samples using Route B

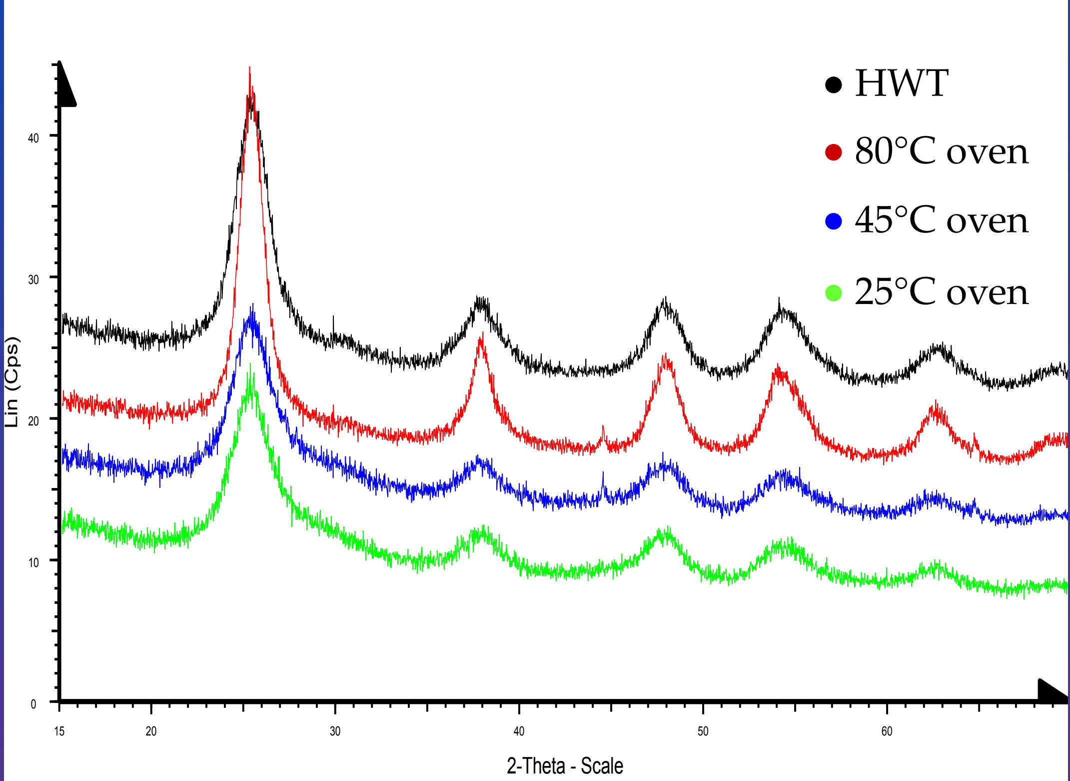




Sample	Crystalline phase	Av. Size of crystallites (Ø, nm)
B.1.1	anatase	5,0 HWT
B.1.2	anatase	7,0
B.1.3	anatase	3,5
B.1.4	anatase	1,5
B.2.1	anatase	7,0
B.2.2	anatase	8,5
B.2.3	anatase	5,0
B.2.4	anatase	2,0
B.3.1	anatase	8,0
B.3.2	anatase	8,0
B.3.3	anatase	8,0
B.3.4	*rutile*	6,5

- XRD patterns of samples B: exhibit better defined peaks, belong to the **Anatase** polymorph.
- the higher the Ti concentration, the larger the diameter of crystallites (2.0< Ø< 8.5 nm);
- also the processing temperature influences Ø: the higher the T_{ageing}, the larger the crystallites.

XRPD : samples TTiP 100%



Sample	Crystalline phase	Av. Size of crystallites (Ø, nm)
HWT	anatase	5.0
80°C	anatase	7.0
45°C	anatase	4.0
25°C	anatase	4.0

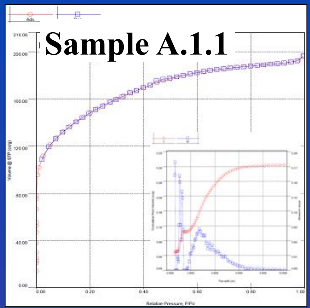
Samples of pure Titania:

- exhibit Anatase phase
- confirm the influence of T on Ø

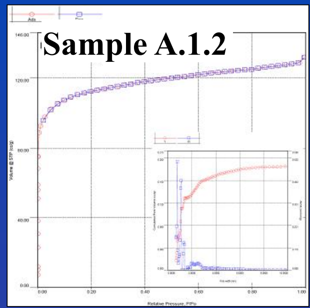
N_2-adsorption analysis

HWT | 80°C | 45°C | 25°C

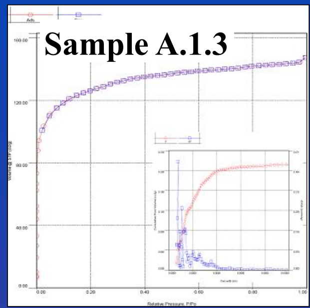
Route A



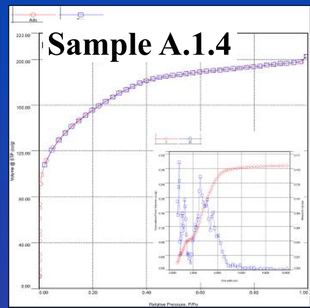
SSA$_{BET}$ = 515 m^2/g
Vol$_{BJH}$ = 0,078 ml/g



SSA$_{BET}$ = 418 m^2/g
Vol$_{BJH}$ = 0,034 ml/g



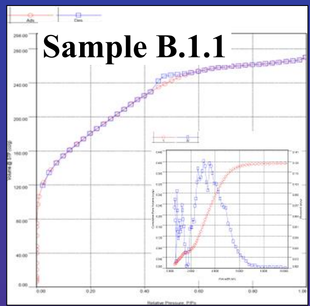
SSA$_{BET}$ = 460 m^2/g
Vol$_{BJH}$ = 0,030 ml/g



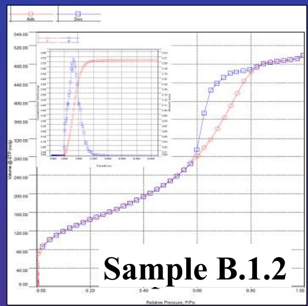
SSA$_{BET}$ = 550 m^2/g
Vol$_{BJH}$ = 0,063 ml/g

The isotherms are generally obtained for <u>microporous</u> materials.

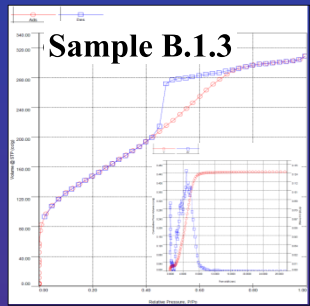
Route B



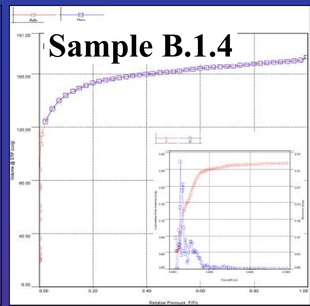
SSA$_{BET}$ = 642 m^2/g
Vol$_{BJH}$ = 0,154 ml/g



SSA$_{BET}$ = 528 m^2/g
Vol$_{BJH}$ = 0,715 ml/g



SSA$_{BET}$ = 532 m^2/g
Vol$_{BJH}$ = 0,316 ml/g

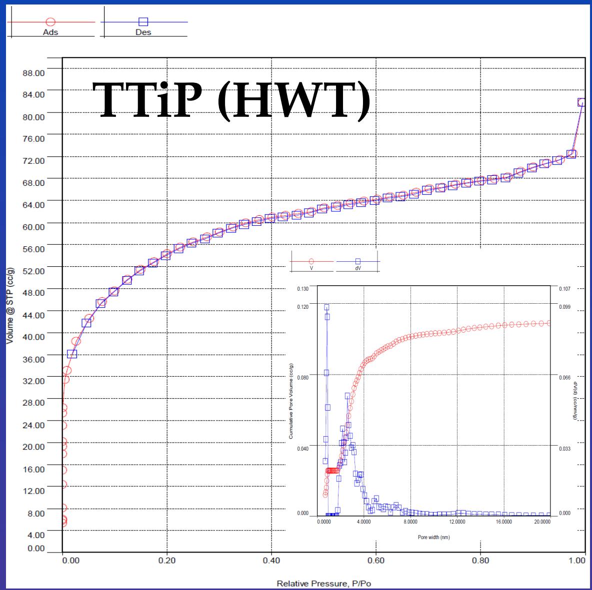


SSA$_{BET}$ = 558 m^2/g
Vol$_{BJH}$ = 0,031 ml/g

Isotherms (T>25°C) typical for <u>mesoporous</u> materials.

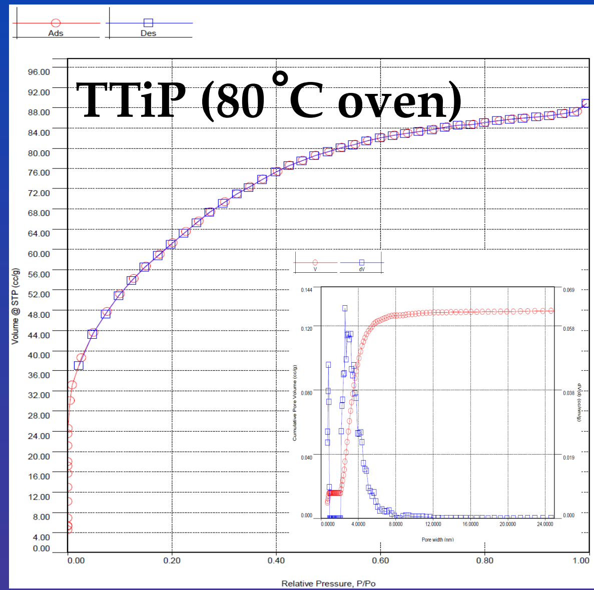
- DFT pore distributions of samples B1.1, B1.3 show a bimodal micro/meso porous distribution; pore volume values are larger than those of the corresponding microporous samples.
- samples A (T > 25°C) possess SSA$_{BET}$ values in the 420 - 520 m^{2}g^{-1} range, while samples B (T > 25°C) possess larger SSA$_{BET}$ values, up to 640 m^{2}g^{-1}.

N_2-adsorption analysis : samples TTiP 100%



$SSA_{BET} = 193\ m^2/g$

$Vol_{BJH} = 0{,}045\ ml/g$



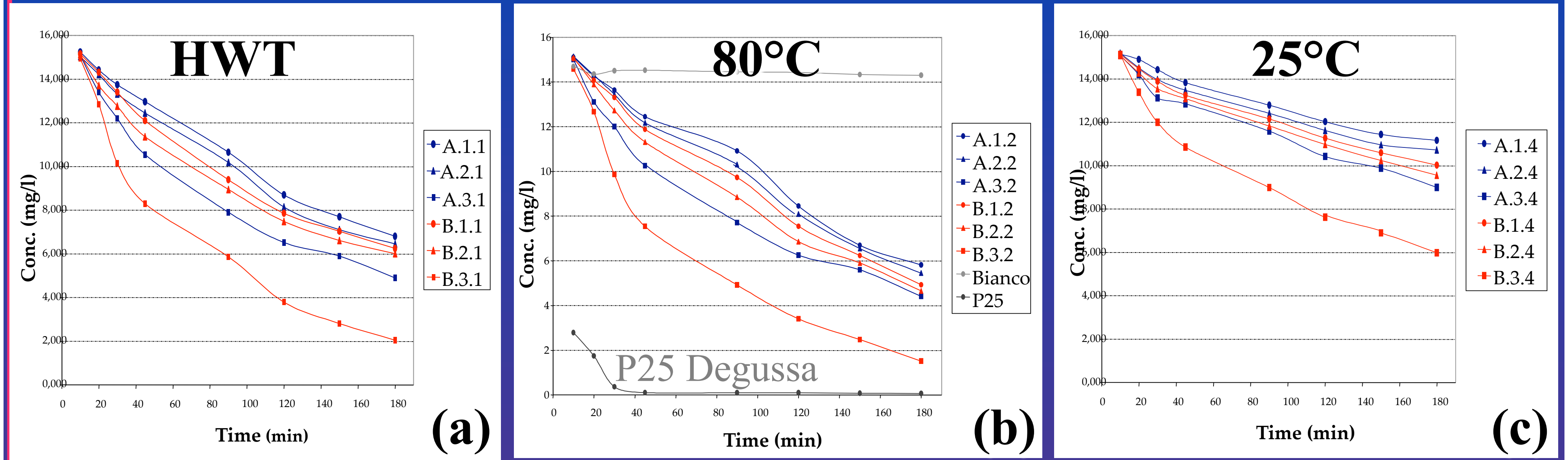
$SSA_{BET} = 221\ m^2/g$

$Vol_{BJH} = 0{,}042\ ml/g$

Samples of pure Titania: in the absence of the porous SiO_2 matrix possess a lower SSA-BET value of about 200 instead of 600 $m^2\ g^{-1}$.

Photoactivity

The mass of nanocomposite powder containing a fixed amount of TiO_2 (25 mg) was added to the aqueous testing solution (35 ml of MB 15 mgL^{-1}):

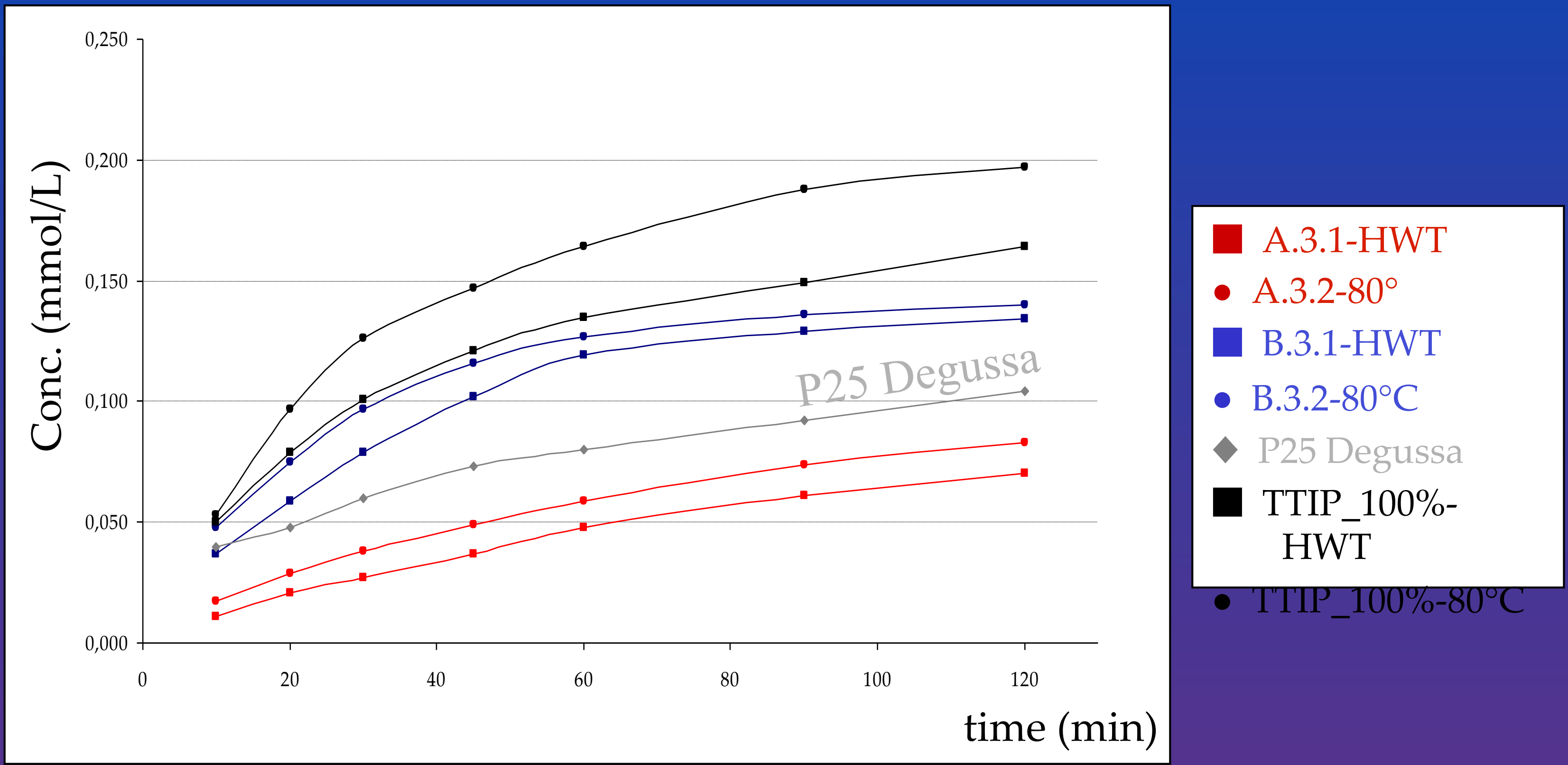


- Samples A possess lower photoactivity in discoloration of MB.
- For powders A.1.1, A.2.1, A.3.1 (HWT), their increased crystallinity, caused by the higher TTIP concentration, results in the increased rates of MB discoloration.
- For samples B, the higher the process temperature and the TiO_2 concentration, the faster the photodegradation of organic dye: the catalyst TEOS/TTIP=50:50-80°C is able to cause the disappearance of 90% of MB in 3 hours.
- the standard Degussa P25 degrades 90% of the dye in just 20 minutes! [4]

[4] *J. Photochem. Photobiol. A: Chem.*, 2001, 139, 253

Photoactivity

The mass of nanocomposite powder containing a fixed amount of TiO_2 (25 mg) was added to the aqueous testing solution (35 mL of 0.1 M KI):



- Tests of photo-induced I_2 formation confirm the trends;
- in this set of experiments, the photo-oxidative efficiency of our SiO_2/TiO_2 powders is higher than that of P25-TiO_2 .

2.3. Preparation of Sols → Coated PES

SiO_2-TiO_2 sols

- *dip (2 min., r.t.)*
- *pad (3.0 kgcm^{-2})*
- *dry-cure process (80°C or **HWT** [5],[6],[7])*

transparent coatings on two different PES fabrics

P1 (standard): 59 gm^{-2}, pick-up= 20%

P2 (commercial): 60 gm^{-2}, pick-up= 69%

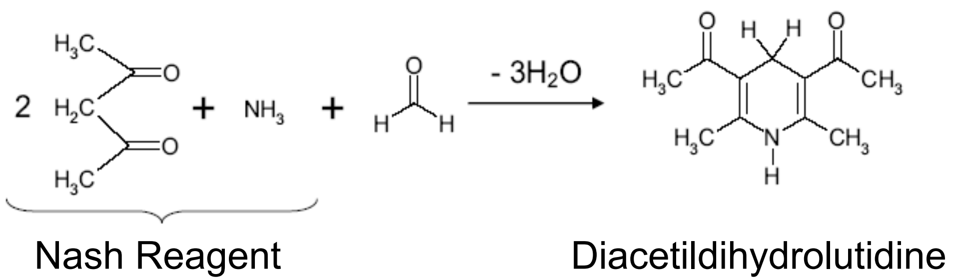
[5] Djaoued, Y. et al. *J. Sol-Gel Sci. Technol*. **2002** 24 247-254.
[6] Matsuda, A. et al. *J. Sol-Gel Sci. Technol*. **2003** 27 61-69.
[7] Daoud, A. et al. *J. Am. Ceram. Soc*. **2004** 5 953-955.

2.4. Coated fabrics characterization

Photoactivity

test method for the photoactivated gas-phase degradation of HCHO

1. glass reactor, v= 18 l (UNI ISO105-G01)
2. textile sample (20 cm x 20 cm)
3. 300W OSRAM UltraVitalux® solar lamp (d=40 cm)
4. mechanical stirrer (170 rpm)
5. three-way valve for gas inlet/output
6. gaseous formaldehyde inlet system
7. 100 ml syringe
8. sample's reactor containing Nash reagent

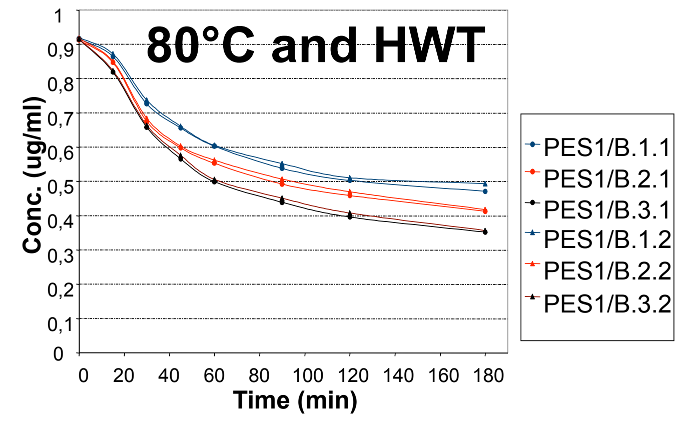


(λ_{MAX} = 412 nm)

Photoactivity: air depollution effect

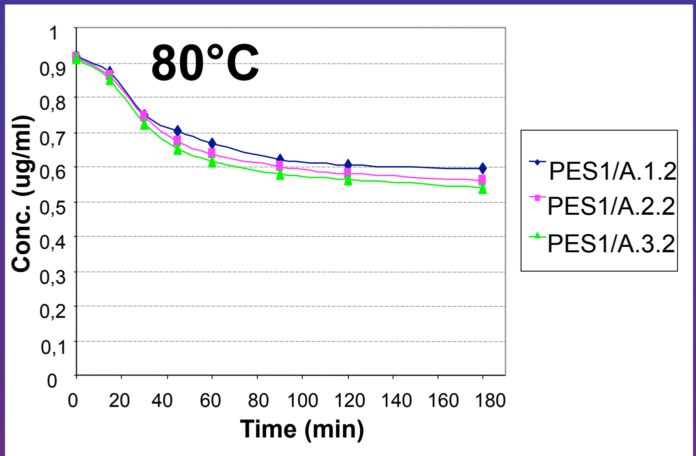
PES_1 (pick-up = 20%)

Coatings B



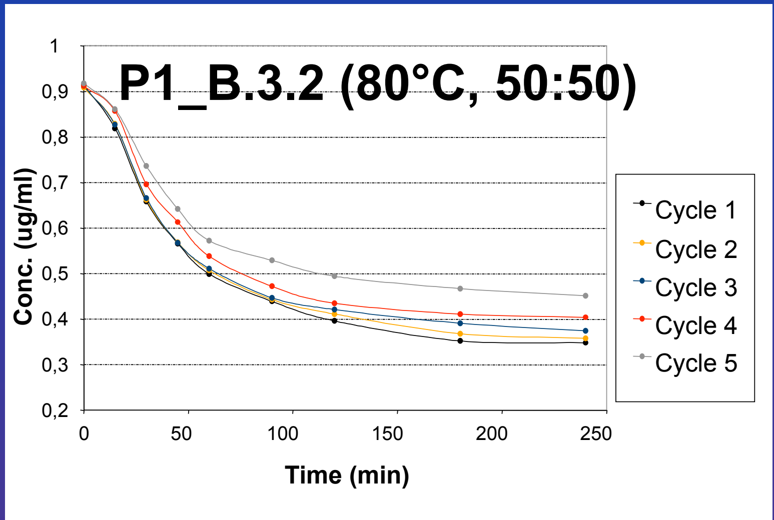
In the case of HWT the disappearance of HCHO is comparable to that obtained with the heating treatment at 80°C.

Coatings A



Lower efficiency of the coatings of type A:
P1/A.3.2 causes a photo-oxidation of 41%
vs
P1/B.3.2 → 62% (3h)

PES_1 (pick-up = 20%)

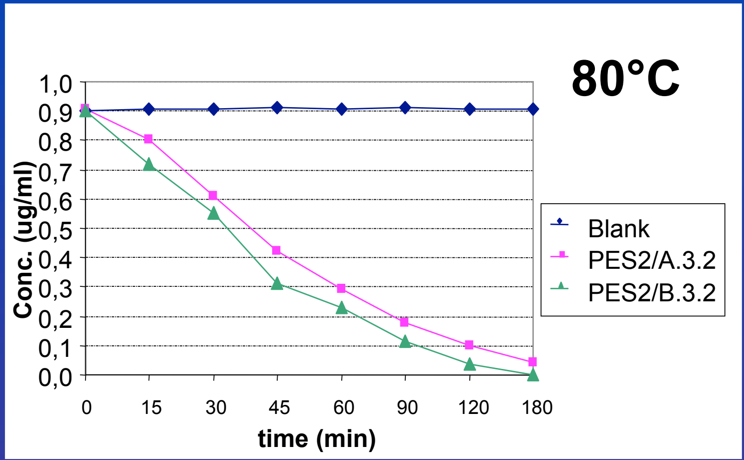


Tested upon five repeated gaseous HCHO photodegradation cycles

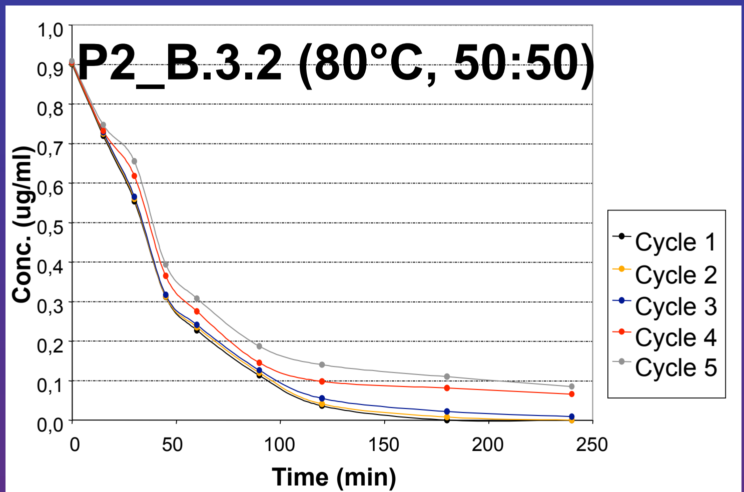
the photocatalytic efficiency on degrading HCHO is reduced from 62% down to 49%.

$$\Delta_{eff.} = -\ 1.9\ \mu g_{HCHO}/cm^2_{TEX}$$

PES_2 (pick-up = 70%)



The higher mass of the SiO_2-TiO_2 coating causes a faster disappearance of formaldehyde: photodegradation of <u>96% occurs in only two hours</u>.



Tested upon five repeated gaseous HCHO photodegradation cycles:

→ the photocatalytic efficiency on degrading HCOH is reduced from 96% to 85%:

$$\Delta_{eff.} = -\,2.3\ \mu g_{HCHO}/cm^2_{TEX}$$

Heating treatment (100°C) allows us to obtain a partial regeneration catalytic eff.

CONCLUSIONS

- The efficiency of the powders extracted from sols depends on the synthetic method and on the treatment T;

  process B, with co-condensation of two alkoxides and the heating at 80°C, represents a simple method to prepare the most efficient photocatalytic materials (mesoporous powders and coatings).

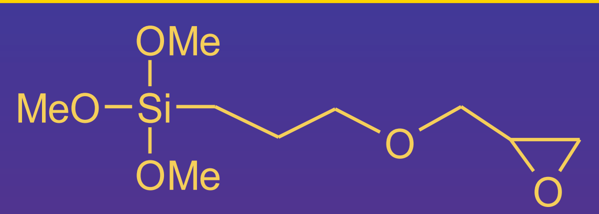
  They have higher crystallinity, presence of anatase and av. crystallite sizes up to 8 nm.

- We showed that a PES with a pick-up of 70% treated with a sol TEOS/TTIP=50:50 is a proper substrate to produce a photocatalytically active fabric with depollution effect.

CONCLUSIONS
and
PERSPECTIVES

- Evaluation of degradative effect of light exposition (XenoTest) on physico-mechanical characteristics of the treated PES fibre.

- Use of GLYMO to improve the adhesion of the functional coating to the fibre's surface.



(3-Glycidoxypropyl)trimethoxysilane

Acknowledgements:

- Project NanoCrystals (no. 2009-9446)

  Uninsubria, SSS, IC-CNR Bari.

  → synthesis of TiO_2 nanocrystals and characterization with new mathematical models.

- Project ANNETTE: ANalysis NEtwork for TExtile,

  Regione Lombardia (bando Competitività 2009)

  Cluster 3: classification Photocatalytic textile Materials through standardized methods.

Thank you for your attention