TECHNICAL UNIVERSITY OF CRETE

SCHOOL OF ARCHITECTURAL ENGINEERING

LABORATORY OF MATERIALS FOR CULTURAL HERITAGE

&

LABORATORY OF ANALYTICAL AND ENVIRONMENTAL CHEMISTRY

"ASSESSMENT OF CHEMICAL COMPATIBILITY AND AMELIORATION OF STONE CONSOLIDANTS WITH NANOTECHNOLOGY"

«ΕΛΕΓΧΟΣ ΧΗΜΙΚΗΣ ΣΥΜΒΑΤΟΤΗΤΑΣ ΚΑΙ ΒΕΛΤΙΩΣΗ ΣΤΕΡΕΩΤΙΚΩΝ ΛΙΘΟΥ ΜΕ ΝΑΝΟΤΕΧΝΟΛΟΓΙΑ»

PhD Thesis

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Chania 2015

Supervisor:

Associate Professor Pagona Maravelaki

Outline of PhD Thesis

1. Introduction – Problem
2. Aim of PhD Thesis
3. Methodology
4. Results – Characterization of the novel nanocomposites
5. Results – Application and evaluation of the nanonocomposites as consolidant protective and self-cleaning coating
6. Conclusions
7. Recommendations for future work

Decay of building construction materials

Causes of Stone Decay

The deterioration of stone originating from the synergistic action of **physical**, **chemical** and **biological** factors which induce sever changes on the **surface** and **structural integrity** of the materials.

Factors as:

- **Air pollution**
- **Water**
- **Salts**
- **Temperature changes**

It is the main factor of stone decay, through direct and indirect mechanisms

Decay of building construction materials

Weathering effect on a sandstone statues in Dresden, Germany

Stone decay of the Fortifications of Aptera, Chania

Stone's biodeterioration due to the development of microorganisms

Necessity of developing novel materials for protection, consolidation and self-cleaning of building materials

Materials with particular criteria

Decay of building construction materials

Restoration materials' criteria:

- **Chemical compatibility**
- **Ease of penetration** and **high penetration** depth
- **Avoidance** of **accumulation** of the material on the stone **surfaces**
- Reduction of the **water permeability** within **acceptable ranges**
- **Avoidance** of alteration of the **chromatic parameters** after the treatment
- **Eco-friendly** and low concentration of Volatile Organic Compounds (VOCs)
- **Friendly** and **convenient** for the **users**
- **Low cost** materials

Decay of building construction materials

Stone Restoration and protection

Materials of Restoration

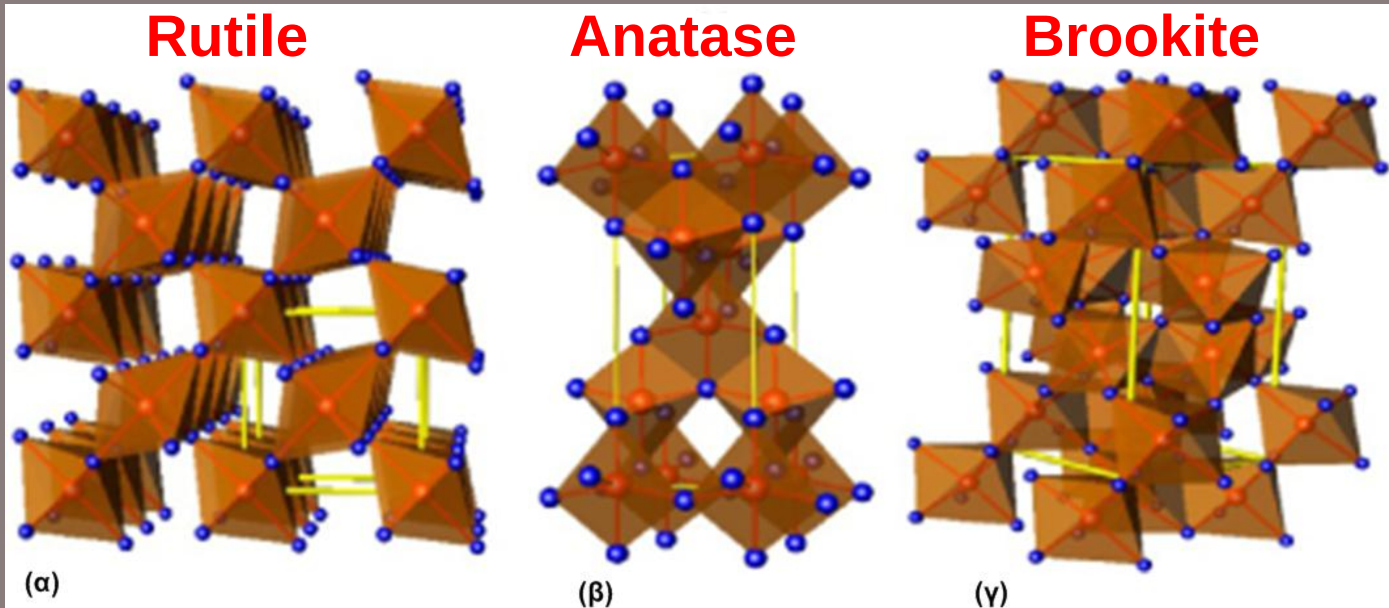
- Alkoxysilane
- Epoxies
- Acrylics
- Fluoropolymers

Commercial restoration Products:

- Consolidants
- Hydrophobic
- Super-hydrophobic
- Self-cleaning
- Biocide

Nanotechnology and restoration materials

Titanium dioxide (TiO_2)



V. C. Fuertes, C. F. A. Negre, M. B. Oviedo, F. P. Bonafé, F. Y. Oliva, and C. G. Sánchez, J. Phys. Condens. Matter, vol. 25, no. 11, p. 115304, Mar. 201

- ✓n-type semiconductor
- ✓High photocatalytic-activity
- ✓Hydrophilicity
- ✓Low-cost nano-material
- ✓Low toxicity
- ✓High chemical and thermal stability
- ✓Insolubility in water

→

Self-cleaning coatings
Purification of water and air systems
Water splitting
Hydrogen production
Solar cells
Hydrophilic-hydrophobic coating
Ink-jet printing

Titanium dioxide (TiO_2)

Synthesis of TiO_2 through the sol-gel process

- Simple experimental procedure and laboratory equipment
- Low temperature
- Low-cost
- Eco-friendly process

Nano-particles with:

✓Homogeneity
✓ High purity
✓High uniformity

Precursor Ti alkoxide

Stages of sol-gel process

1. Hydrolysis of titanium alkoxide
2. Polymerization/poly-condensation

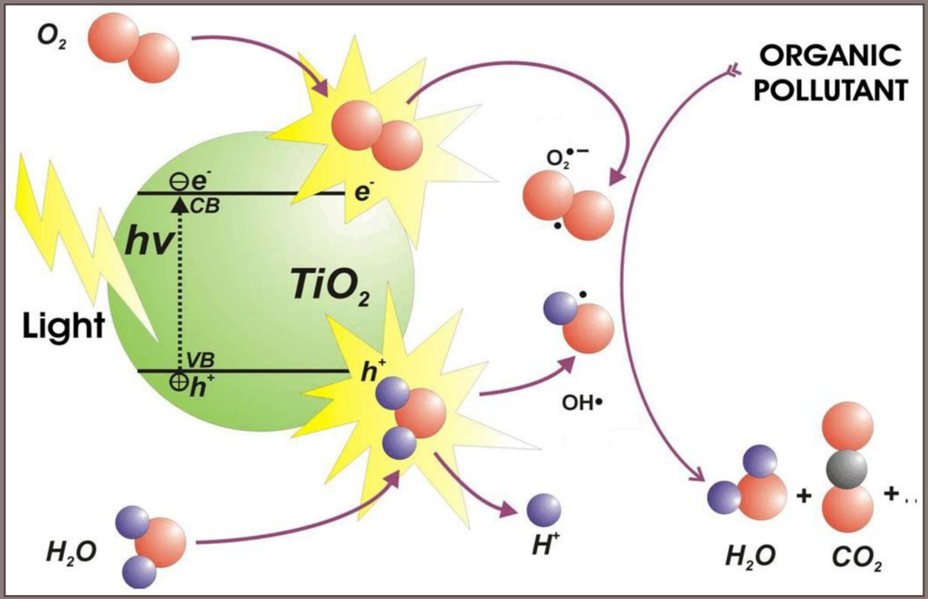
Overall reaction

$$Ti\text{-}(OR)_4 + 2H_2O \rightarrow TiO_2 + 4ROH$$

After sol-gel process the nano-particles were annealed at high temperature in order to produce the photo-active crystalline phases of TiO_2

Titanium dioxide (TiO_2)

Photocatalytic activity



A. Ibhadon and P. Fitzpatrick, Catalysts, vol. 3, no. 1, pp. 189–218, 2013.

Photocatalytic reactions:

$Ti_2O + hv \rightarrow e^-_{CB} + h^+_{VB}$

$e^-_{CB} + h^+_{VB} \rightarrow$ heat (recombination)

$e^-_{CB} + O_{2,ads} \rightarrow O^{\cdot -}_{2,ads}$

$h^+_{VB} + H_2O_{ads} \rightarrow OH^{\cdot}_{ads} + H^+$

$h^+_{VB} + OH^-_{ads} \rightarrow OH^{\cdot}_{ads}$

$h^+_{VB} + RH_{ads} \rightarrow R^{\cdot}_{ads} + H^+$

$OH^{\cdot} + R_{ads} \rightarrow \rightarrow \rightarrow CO_2 + H_2O$

Anatase >>Rutile

Stage of photocatalytic procedure:

1st Adsorption of oxidizing and reducing agents on TiO_2 surface
2nd Oxidation and reduction reaction on TiO_2 surface
3rd Disposal of the final products

SiO_2-TiO_2 nanomaterials for stone restoration

Alkoxysilanes

Base of the products for consolidation and protection

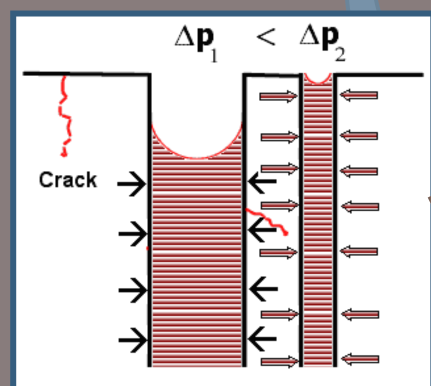
Advantages

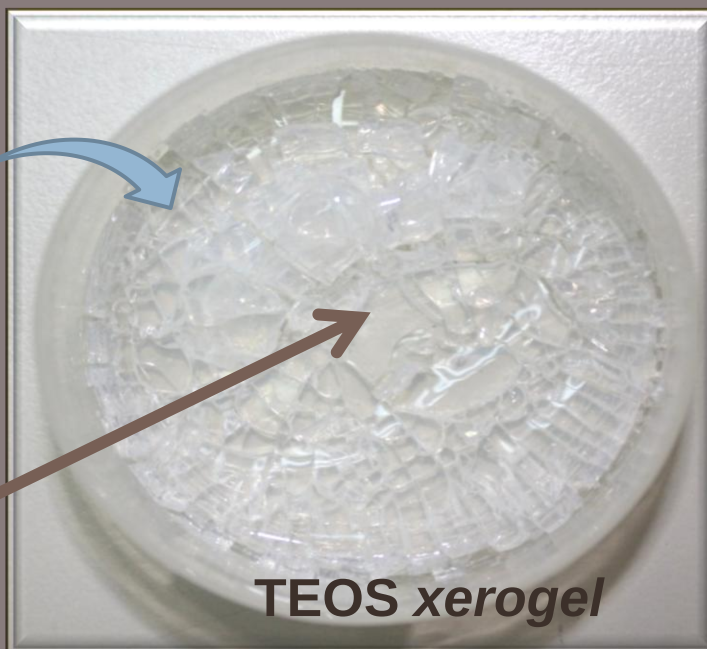
- Their low viscosity facilitates its penetration into the intergranular network of the stone
- Hydrolyse and polymerize *in situ* inside the pore structure

through the sol-gel process

Drawbacks

- Crackings during the xerogel formation



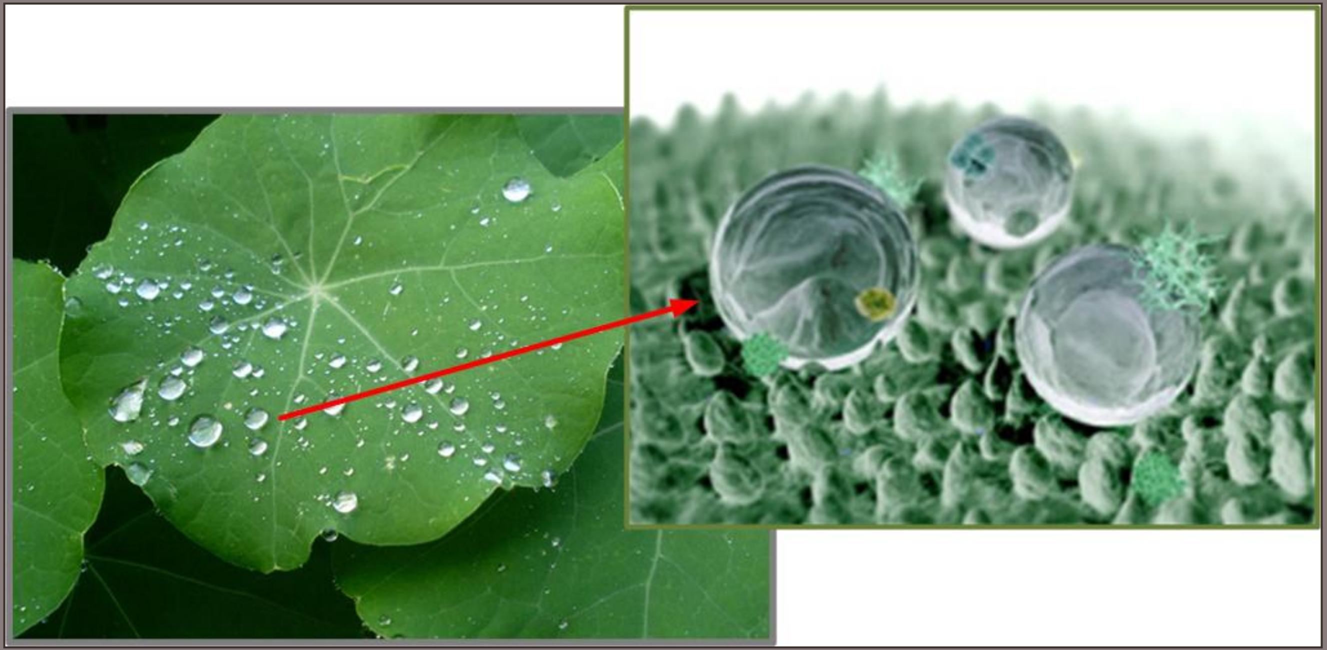


SiO_2-TiO_2 nanomaterials for stone restoration

Hydrophobocity

Hydrophobic surfaces: > 90º
Super-hydrophobic: >150º

Bio-inspired hydrophobic and super-hydrophobic surfaces as ***Lotus effect*** find application in protection of the building materials



CA

Addition of an Organosilane

http://lotusrock.com/what-is-lotus-rock/
http://www.dec.ny.gov/pubs/56478.html/

Aims of Thesis

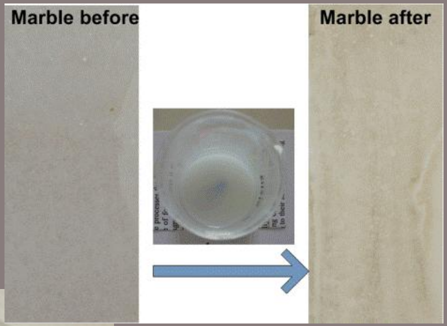
- Synthesis homogeneous colloidal solutions SiO_2-TiO_2 with low viscosity in order to facilitate the penetration into the pores of the stone
- Synthesis of transparent with cohesive structure nanomaterials with protective and self-cleaning properties
- Synthesis of photo-active nanomaterials without any demand of specific laboratory equipment and high temperature
- Synthesis of effective protective, consolidant and self-cleaning coatings for stone applications
- Assessment of chemical compatibility of nanometrials with stones

Aims of Thesis

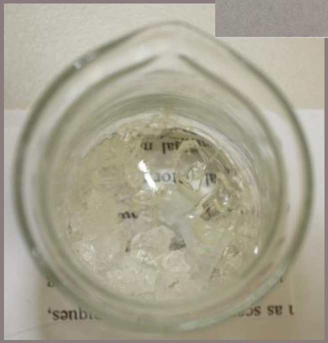
To Overcome problems as:

- Inhomogeneous colloidal solutions and xerogels originating from mixing Si and Ti alkoxides
- **Two phases of** xerogel originating from mixing Si alkoxide and organosilane

- Formation of TiO_2 nano-particles with large size and aggregates, resulting in white colloidal solutions



- Crystalline TiO_2 nanoparticles after annealing at high temperature
- Xerogels with crackings



Methodology

Synthesis of SiO_2-TiO_2-PDMS nano-materials

Syntheses were based on mixing :

Experimental design

- silica alkoxide (Tetra Ethyl OrthoSilicate, **TEOS**)

Precursor material of silica network Si-O-Si

Low viscosity and polymerization into the pore system

Drawback: cracking formation

- titanium alkoxide (Titanium Tetra-IsoPropoxide, **TTIP**)

Precursor of TiO_2

1. Photocatalytic properties
2. Particle Modified Consolidants, PMCs (uniform pores, **absence of crackings**)

❖Control of hydrolysis of Ti alkoxide

❖Pre-synthesized TiO_2 ⇒ white color

Synthesis of SiO_2-TiO_2-PDMS nano-materials

Experimental design

- organosilane (Hydroxyl-terminated PolyDiMethylSiloxane, **PDMS**)

-OH edge for connection with silica network

Hydrophobicity through the inversion of the hydrophilic character of SiO_2-TiO_2 system

and

Cohesive structure

Synthesis of SiO_2-TiO_2-PDMS nano-materials

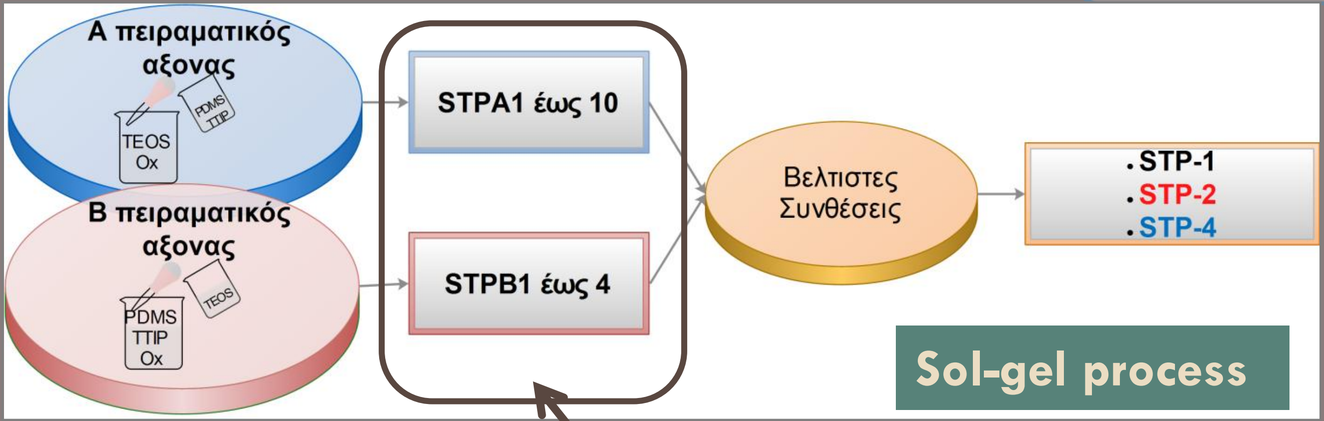
➢Oxalic acid (**Ox**): Compatibility with calcareous stone

1. **Catalyze** the TTIP and TEOS hydrolysis
2. Promote the **formation** of homogeneous colloidal solutions
3. Function as **DCCA**, promoting crack-free xerogels
4. **pH<6**, IEP $\text{Ti-OH} + H^+ \leftrightarrow \text{Ti-OH}_2^+$

   $\text{Ti-OH} + OH^- \leftrightarrow \text{Ti-O}^- + H_2O$
5. **Hole-scavenger**
6. React with calcium carbonate, producing **calcium oxalate** (more stable and weather resistant)

Synthesis of SiO_2-TiO_2-PDMS nano-materials

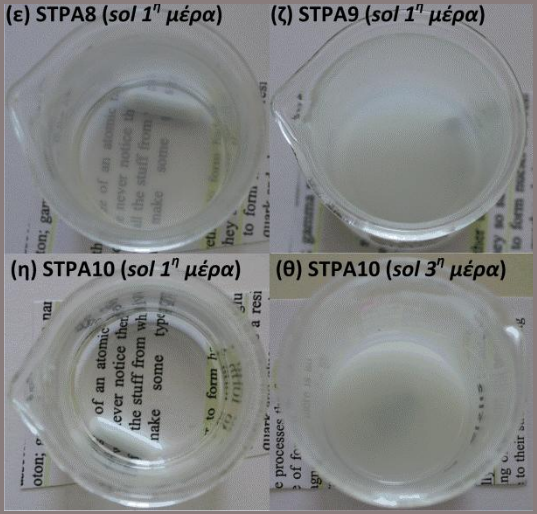
Experimental design



<u>Macroscopic study of the nanomaterials:</u>

- Gelation time
- Low energy footprint
- Presence of cracking in the xerogels

- Transparency



Synthesis of SiO_2-TiO_2-PDMS nano-materials

Experimental design

Optimal syntheses

STP-1 → (A' experimental axis)

STP-2
STP-4 → (B' experimental axis)

Name of the materials

Silica-**T**itania-**P**DMS → STP

Concentration of Ox:

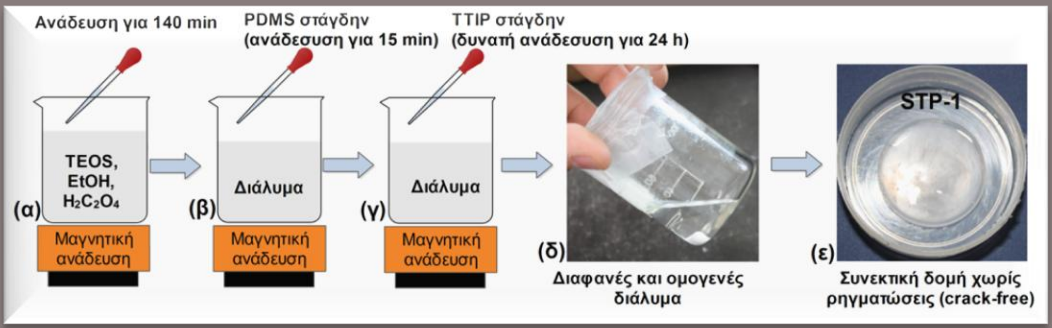
1 low
2 medium
4 high

Synthesis of SiO_2-TiO_2-PDMS nano-materials

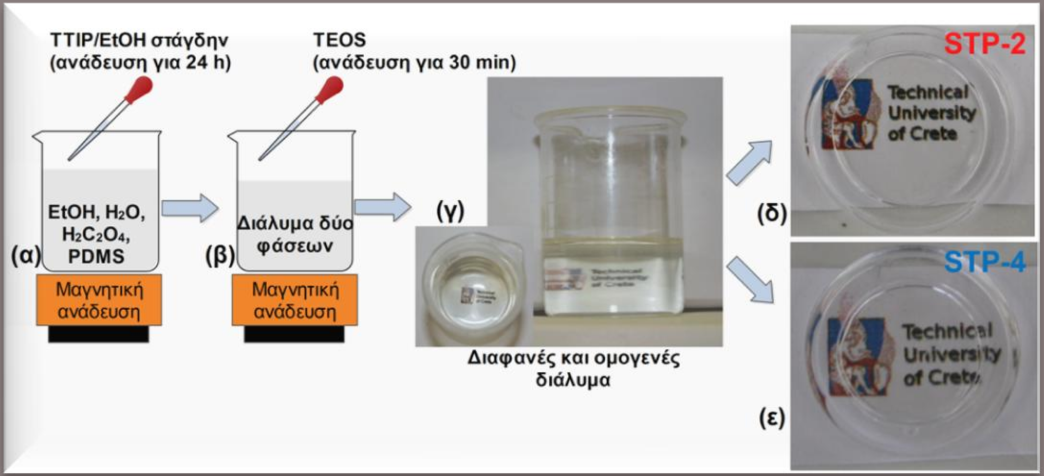
Experimental design

(TEM,N2)

High stirring



Slow addition of TTIP



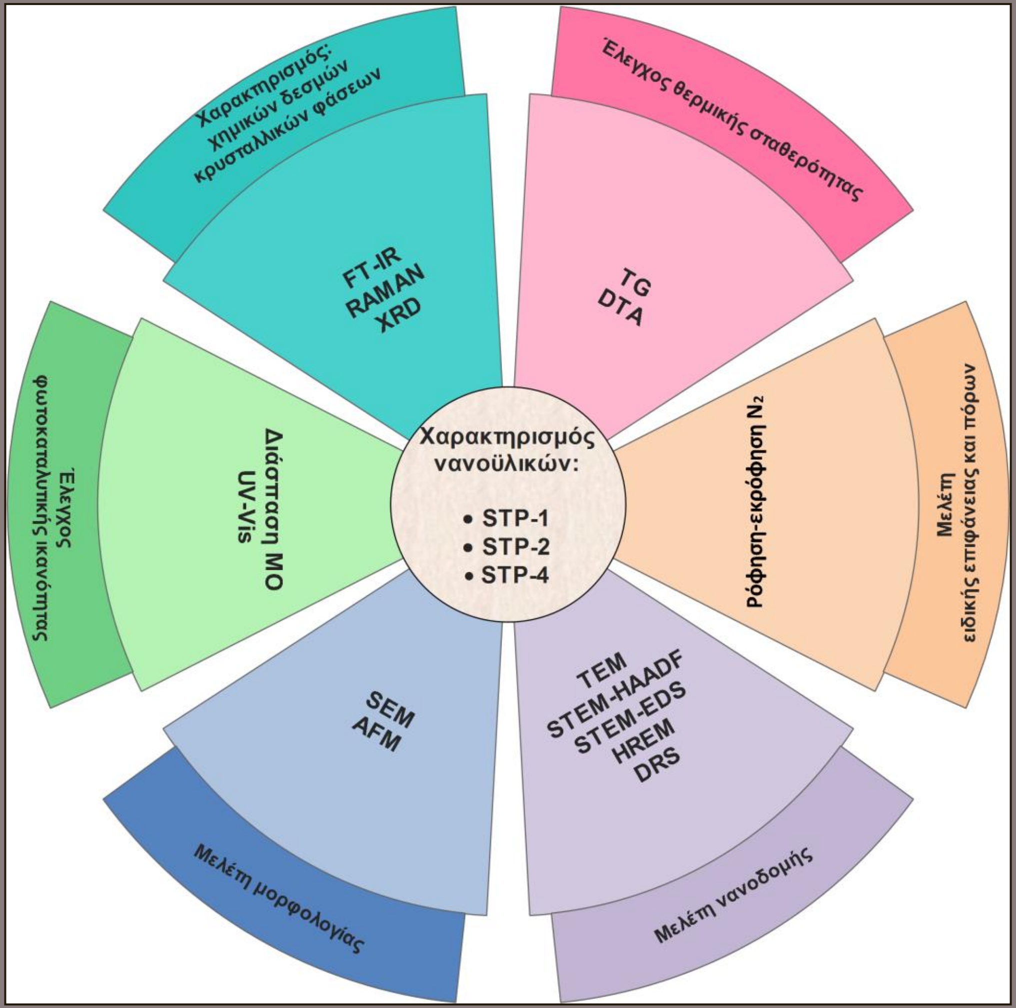
Νανοϋλικό	$H_2C_2O_4$ moles*
STP-1	0.0001
STP-2	0.017
STP-4	0.036

*Referred to1 mol of TEOS

TEOS/EtOH/H_2O/PDMS/TTIP
1/4/4/0.04/0.017

Synthesis of SiO_2-TiO_2-PDMS nano-materials

Experimental design



Results of nanomaterials' characterization

Part A

Results of nano-materials' characterization

Macroscopic characterization

Nano-material	Gelation time (days)	
	Open vessel	Closed vessel
STP-1	5	35
STP-2	9	45
STP-4	5	7

✓STP-2>STP-4 due to the presence of oxalic acid as catalyst
✓STP-1≈STP-4 and STP-1<STP-2(closed vessel) even though the lower concentration of Ox
but they can not be compared (different experimental Axes)

✓Sequence of the reagents
✓Ox concentration
✓STP-2>STP-4 due to the presence of oxalic acid as catalyst

Results of nano-materials' characterization

Macroscopic characterization

Nano-material	% Volume reduction
STP-1	82
STP-2	86
STP-4	84

% Shrinkage (from 82 to 86%)

✓PDMS chains coiled up due to the stress, thus creating high values of shrinkage. These coiled chains present a high elasticity and give flexibility to the xerogels

According to already published results

Results of nano-materials' characterization

Macroscopic characterization

- ✓Colorless
- ✓Homogeneous
- ✓Highly transparent
- ✓Cohesive and crack-free structure

TEOS

Results of nano-materials' characterization

There are difficulties in synthesing **homogeneous** and **transparent** xerogels from mixing alkoxides due to:

- Different hydrolysis rate of the Ti and Si alkoxide

$Si(OR)_4 < < < Sn(OR)_4 \approx Ti(OR)_4 < Zr(OR)_4 \approx Ce(OR)_4$

Unsaturation degree is 0

Unsaturation degree is 2

- Direct precipitation of -Ti-(OH)

Phase homogeneity can be improved by:

1. Pre-hydrolysation of the Si-alkoxide (TEOS)

2. Deceleration of the fast reacting Ti-alkoxide precursor via chemical modification with nucleophilic group (as a chelating ligands)

3. Utilization of single-source precursors.

Results of nano-materials' characterization

Macroscopic characterization

Homogeneity - Transparency

In syntheses STP-1, STP-2, STP-4 the oxalic acid plays the important role for producing homogeneous and transparent colloidal solutions:

(i) Oxalate ion is a **bidentate ligand**, strong **nucleophilic reagent** and **is coordinated** with Ti alkoxide, thus **delaying** the Ti alkoxide hydrolysis and **restricts** the direct precipitation of titanium hydroxide

(ii) Ox acts as **catalyst** of the TEOS hydrolysis

(iii) Ox **prevent the agglomeration** of TiO_2 particles by removal from the IEP as pH ≈ 2

Results of nano-materials’ characterization

Macroscopic characterization

Chemical modification of Ti-alkoxide by Ox

Slow rate of Ti-alkoxide addition in the H_2O/PDMS/Ox (STP-2, STP-4)

Vigorous stirring (STP-1)

Homogeneity - Transparency

Results of nano-materials' characterization

Macroscopic characterization

Homogeneity

The xerogels STP-1, STP-2, STP-4 are **homogeneous** and **monolithic**

↓

This predicts the incorporation of **hydroxyl-terminated** PDMS into the silica matrix and the probable compolymerization between PDMS and TEOS

A two phases xerogel:

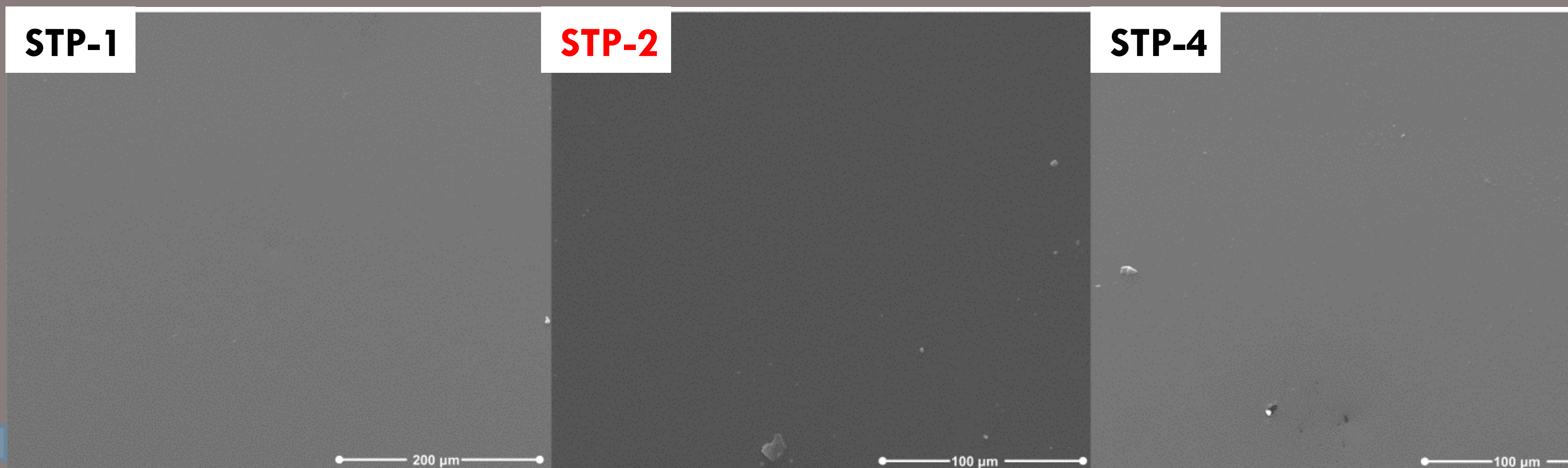
1. **self-condensation of PDMS**
2. **Independent hydrolysis and condensation of TEOS**

Results of nano-materials' characterization

SEM analyses

It is verified the:

✓cohesive and crack-free structure



Synergistic action of **Ox** and **PDMS**

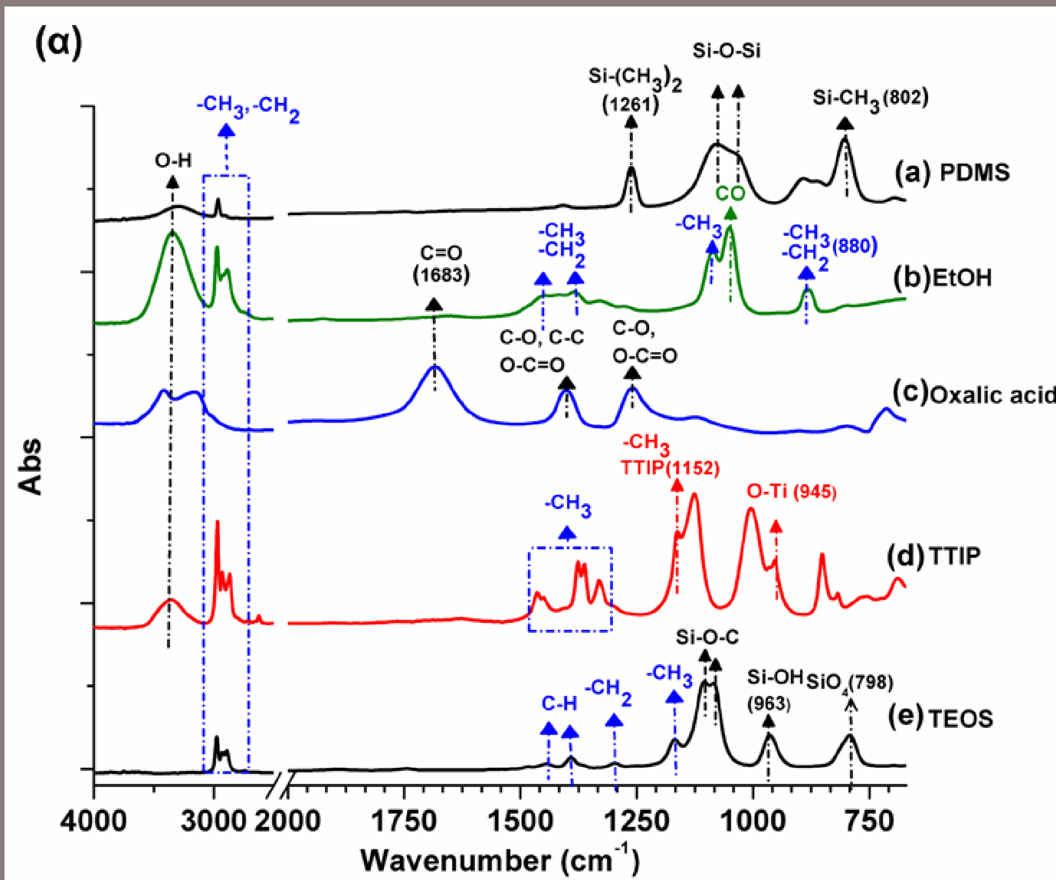
✓Ox as DCCA

✓PDMS
reduce the surface energy with its incorporation into the silica network (toughness and flexible xerogels)

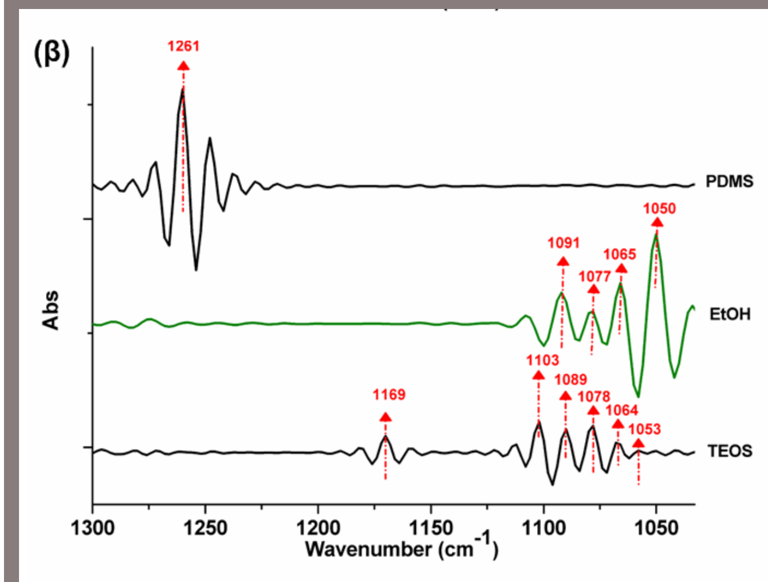
Results of nano-materials' characterization

Raw materials

Infrared Spectroscopy (FTIR)



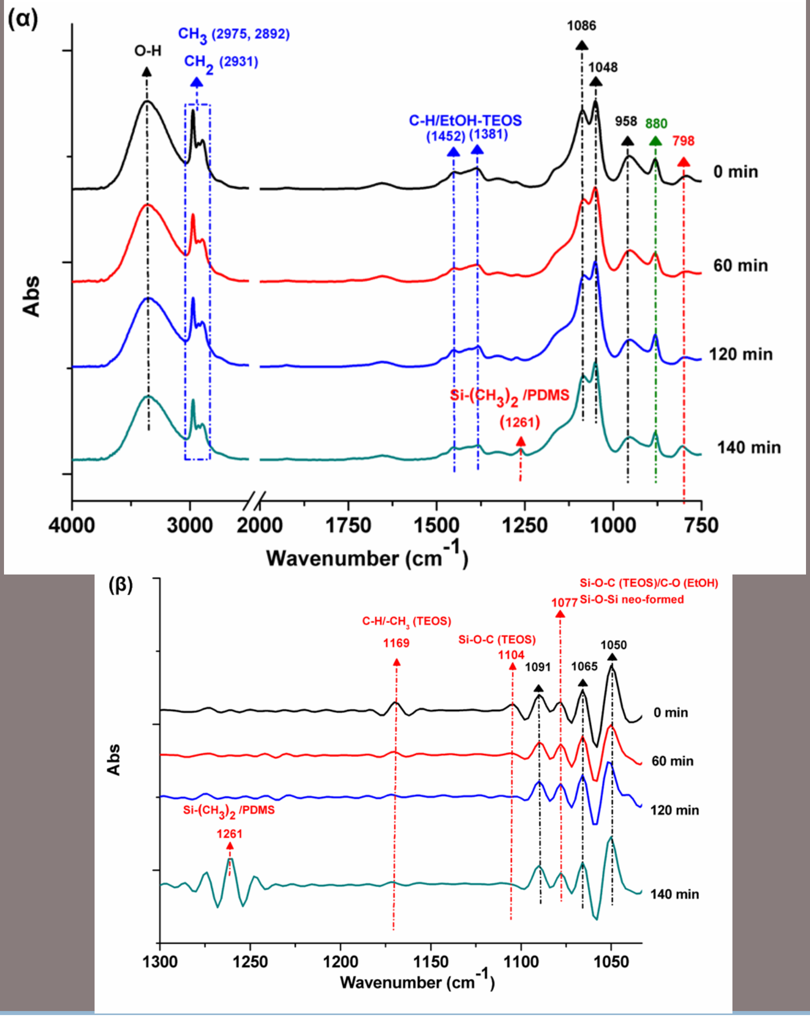
Deconvolution spectra

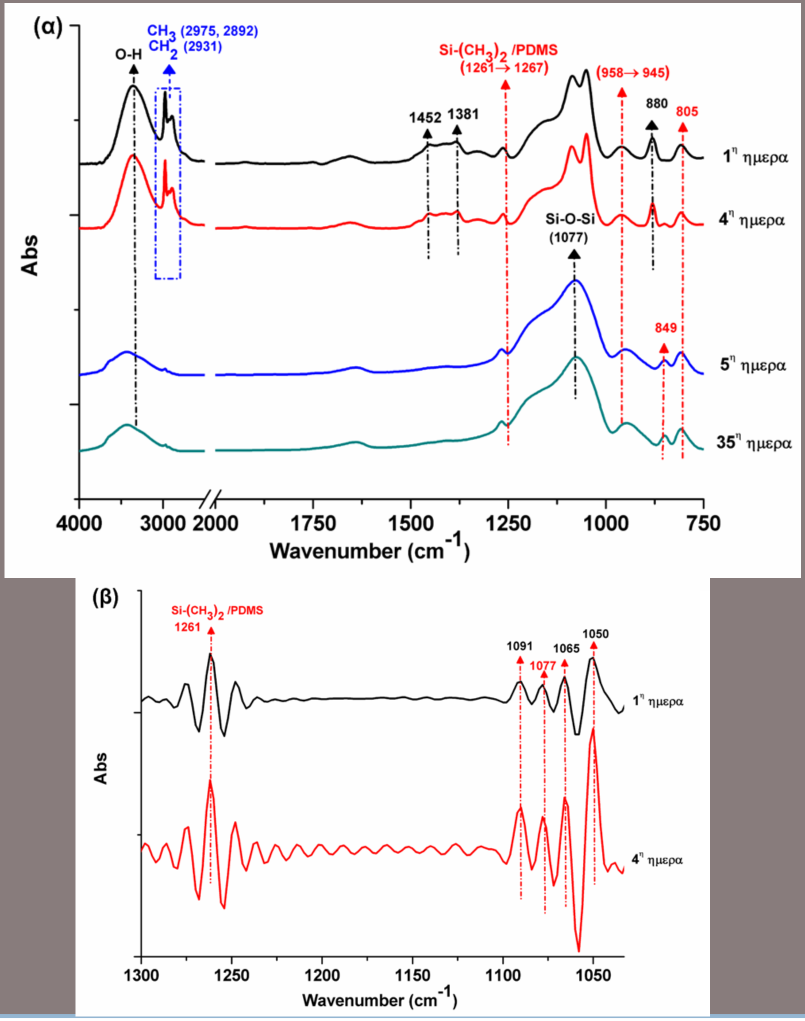


Results of nano-materials' characterization

STP-1

Infrared Spectroscopy (FTIR)

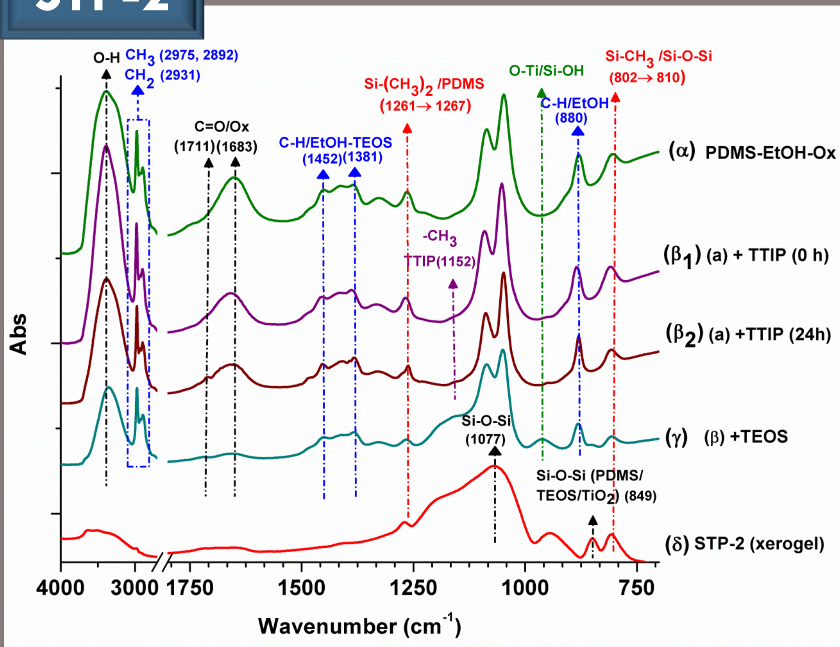


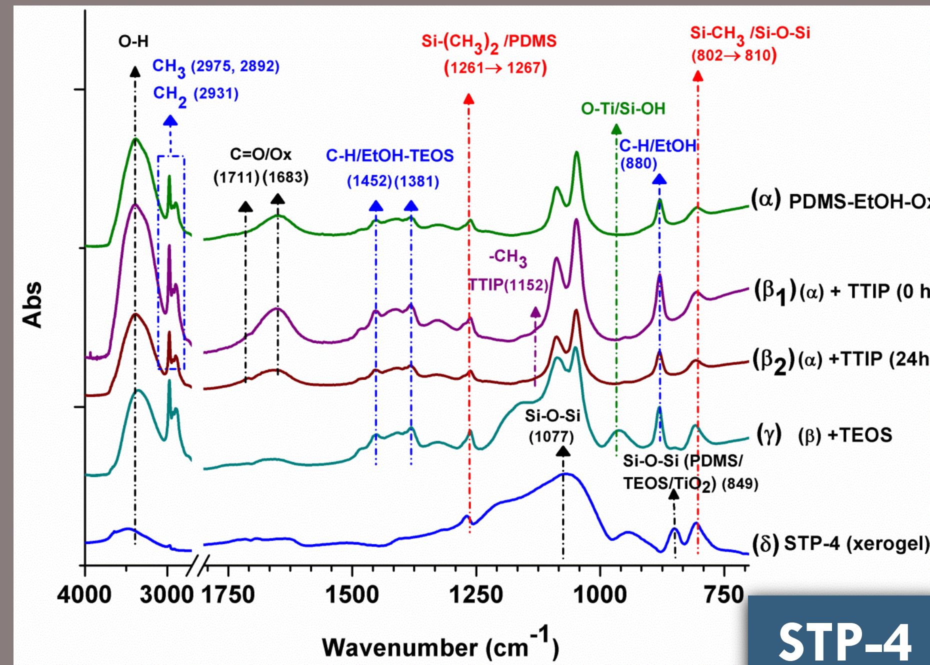


Results of nano-materials' characterization

Infrared Spectroscopy (FTIR)

STP-2



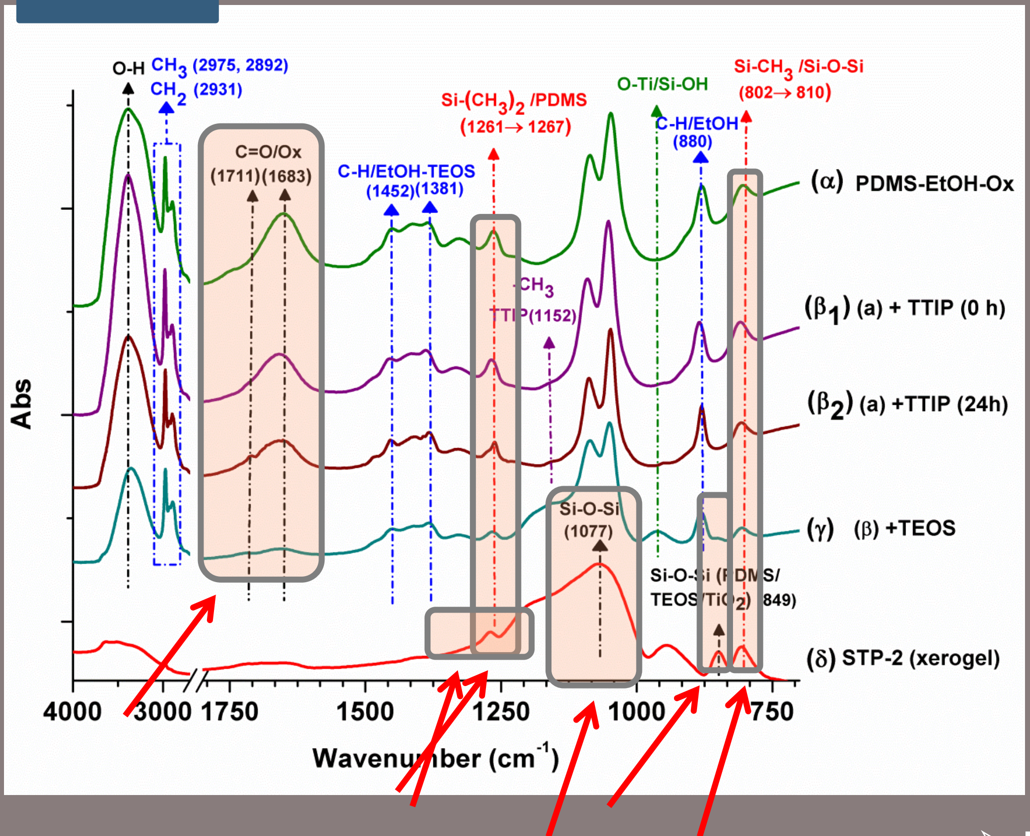


STP-4

Results of nano-materials’ characterization

STP-1, STP-2 and STP-4

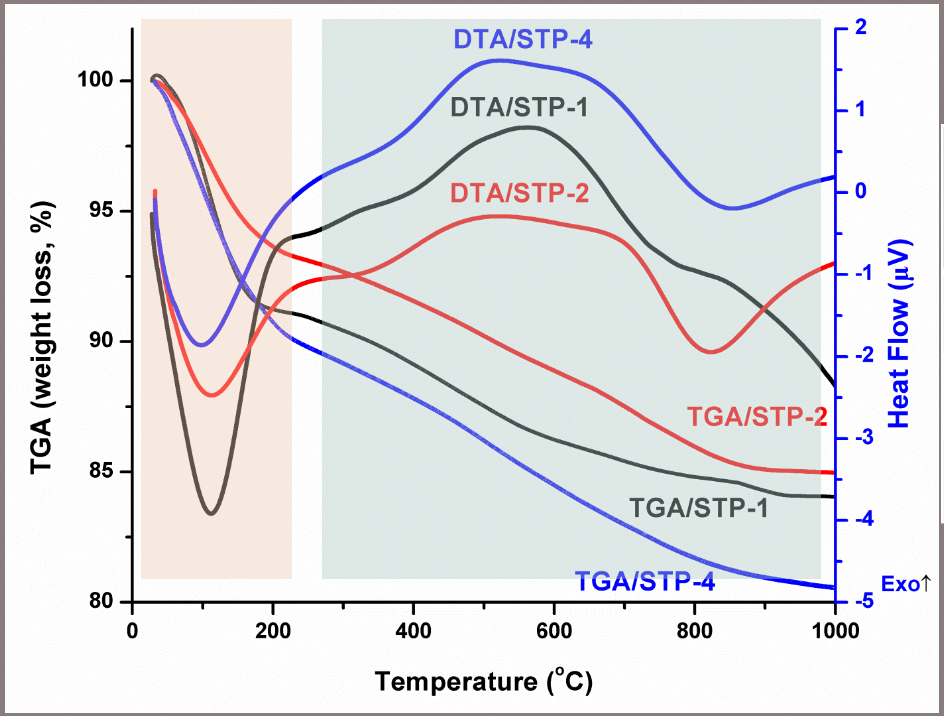
STP-2



- It is confirmed the fully hydrolysis of TEOS from the disappearance of characteristic peaks and appearance of the newly bonds (Si-O-Si)
- Copolymerization of PDMS and TEOS through the shifting of characteristic peak and the appearance of a new peak
- The basic peak 1261 cm^{-1} of PDMS denotes the hydrophobic character of the xerogels
- Probable incorporation of TiO_2 into the silica (STP-1)
- It is confirmed the role of Ox as chelating nucleophilic **reagent**

Results of nano-materials’ characterization

Thermal Analyses



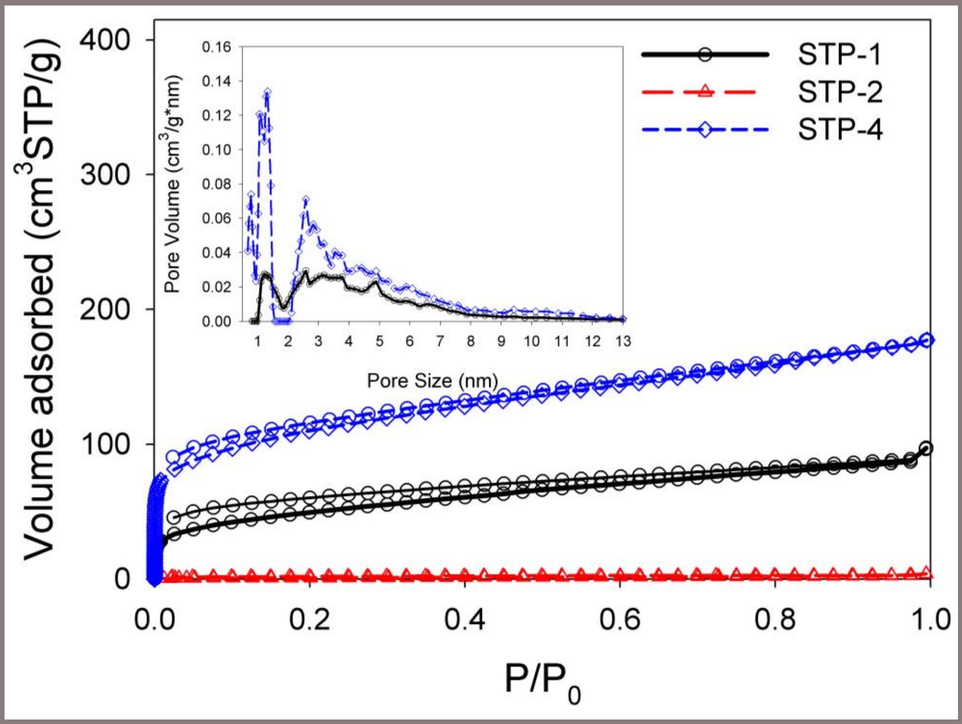
Nano-material	40-200 °C	206-950 °C
STP-1	9	7
STP-2	10	8
STP-4	7	10

Endothermic peak
Absorbed water

Removal of organic solvents and thermal decomposition of organic compounds.
This demonstrates the incorporation of organic parts into the silica network

Results of nano-materials' characterization

Nitrogen adsorption/desorption



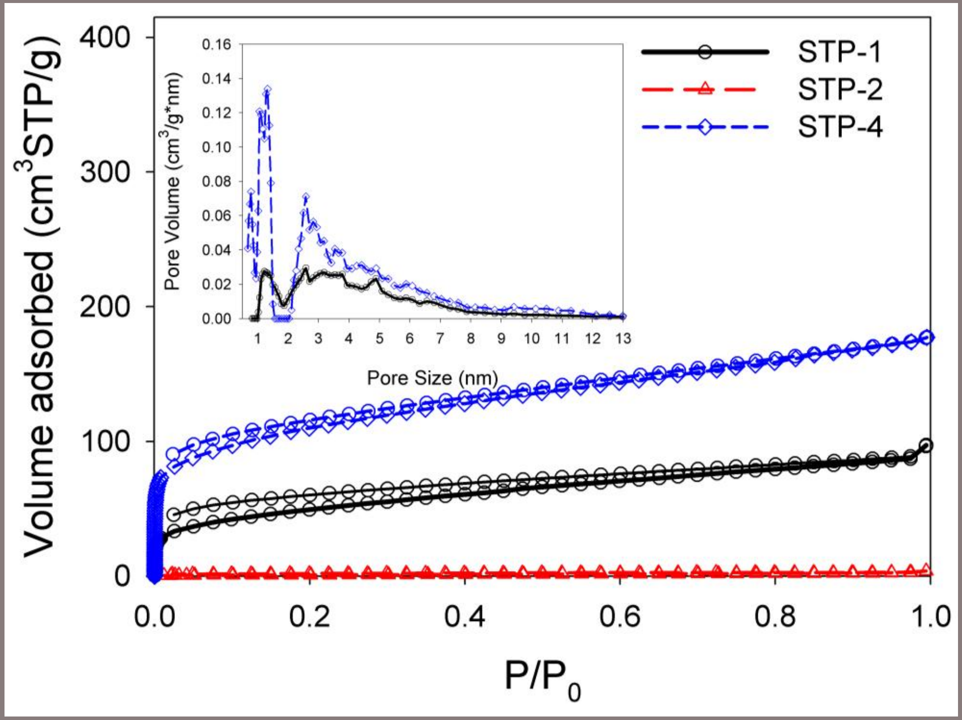
TEM

Nanomaterial	S_{area} (m^2/g)	V_{pore} (cm^3/g)
STP-1	153	0.136
STP-2	3	0.006
STP-4	440	0.260

Pore Volume and Surface Area
STP-1 < STP-4

Results nano-materials' characterization

Nitrogen adsorption/desorption



- The isotherms of STP-1 and STP-4 are **type IV**

⬇

mesoporous materials

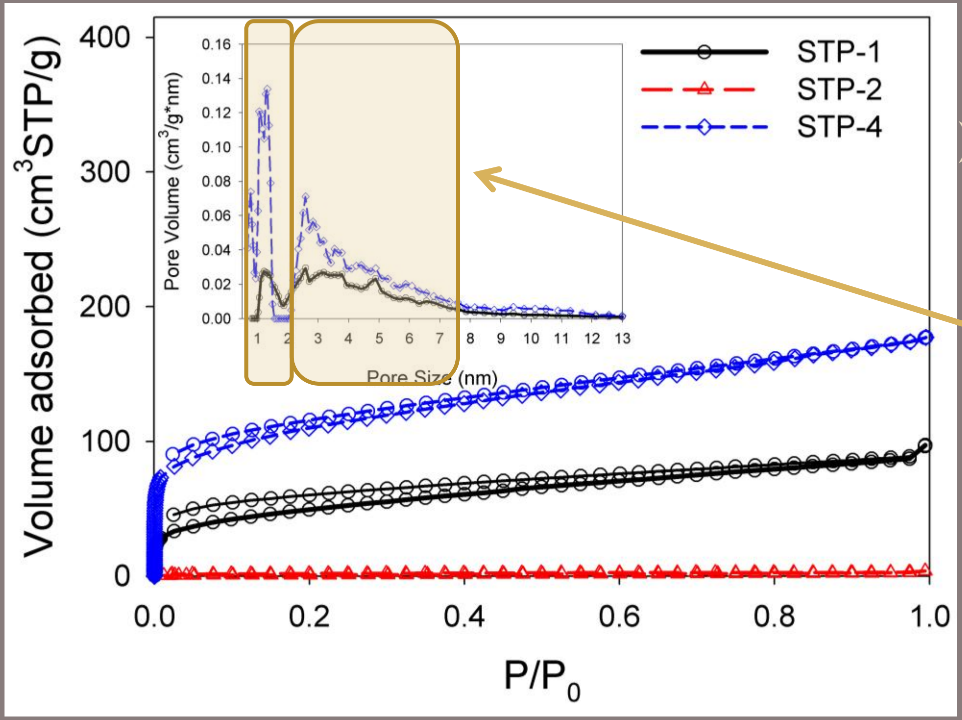
- These materials show a type H4 hysteresis loop characterized by parallel and almost horizontal branches

⬇

- Materials composed of particles with **internal voids** of **irregular shape** and **broad size distribution**.
- **Large mesoporous embedded in a matrix with pores of much smaller size**

Results of nano-materials' characterization

Nitrogen adsorption/desorption

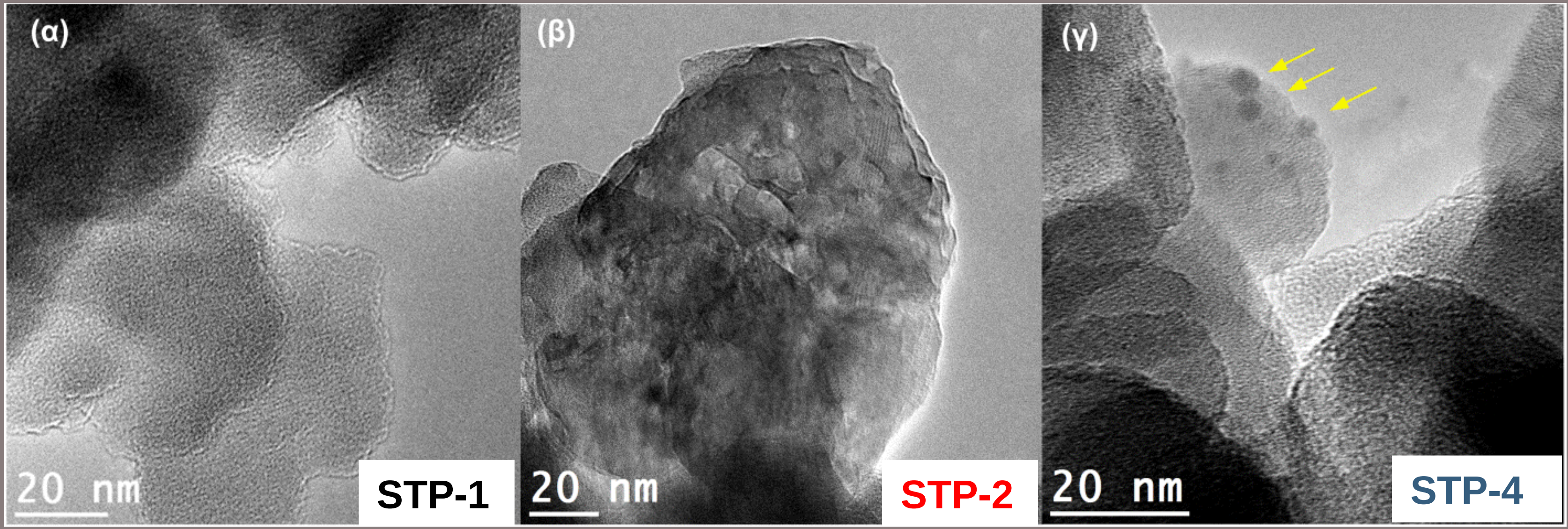


- NLDFT method in order to obtain the pore size distribution

Covering both:
micropores (from 1 to 2 nm) and mesopores (from 2 to 50 nm)

Results of nano-materials' characterization

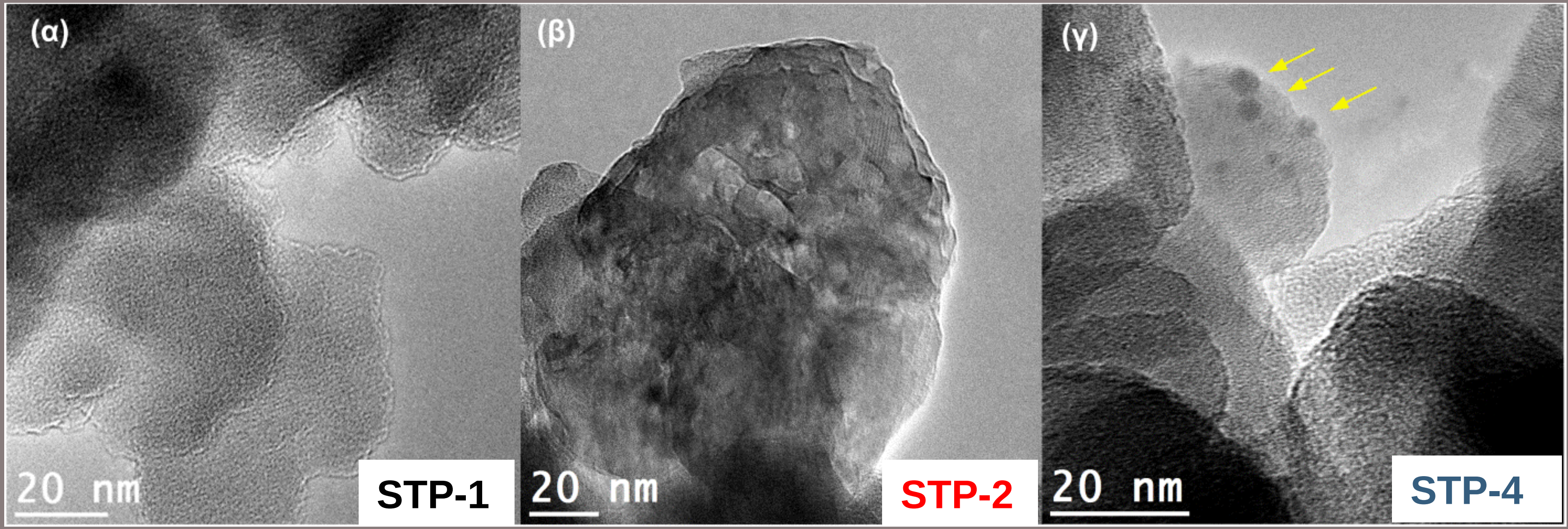
TEM



- Significant differences between STP-1 and the other materials
- STP-1 presents uniform and cohesive SiO_2-TiO_2-PDMS network with aggregates 40-100 nm
- The observed chemical structure of STP-1 demonstrates the formation of bonds Ti-O-Si in atomic level

Results nano-materials' characterization

TEM

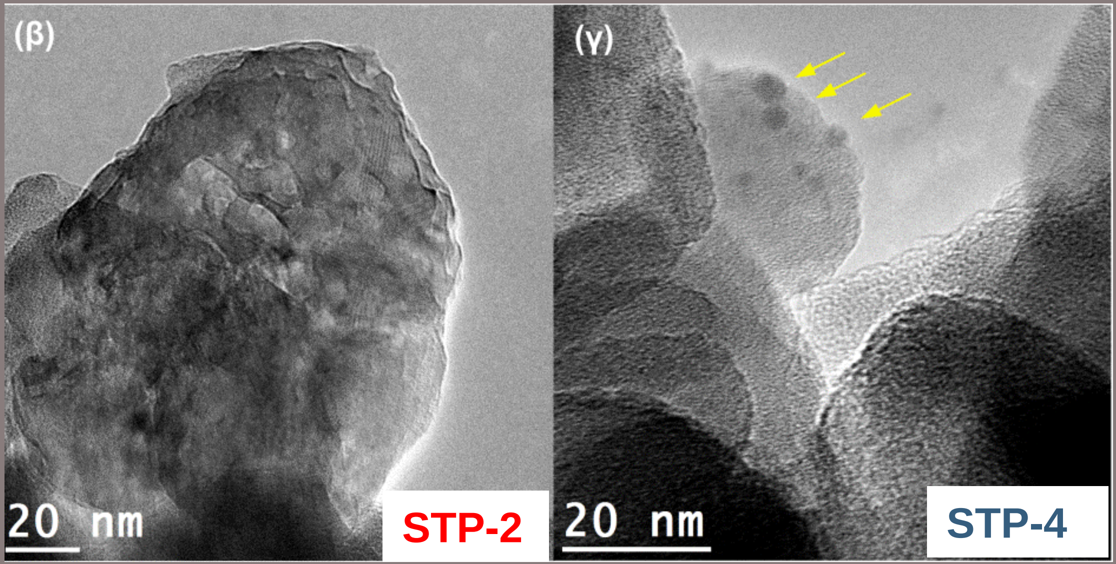


- STP-2 and STP-4 show aggregates of similar size as STP-1
- **BUT** in STP-2 and STP-4 nanoparticles of TiO_2 incorporated into the SiO_2 matrix can be observed
- STP-1 and STP-4: show medium compact texture (with pores) STP-2: the texture is dense (without pores)

Results of nano-materials' characterization

TEM

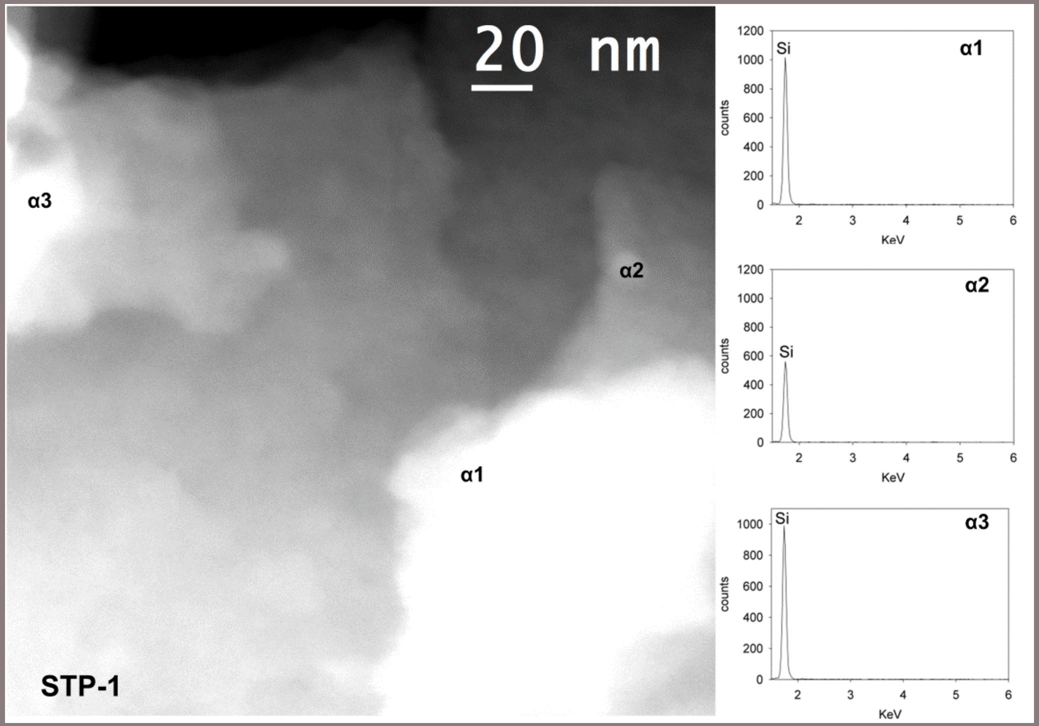
Differences in **particle sizes** and **amounts**



Comparison of **STP-2** and **STP-4**

- In STP-4 (high Ox), the TiO_2 nanoparticles with smallest size (ranging from **2 to 5 nm**)
- In STP-2 (medium Ox), the TiO_2 nanoparticles with larger size (ranging from **5 to 10 nm**) and aggregates inside the matrix
- Much more higher TiO_2 content is present in separate domains for STP-2

Results of nano-materials' characterization



STEM-HAADF

- It does not present any difference in contrast across the material

Bonds Ti-O-Si in atomic level

X-EDS spectra

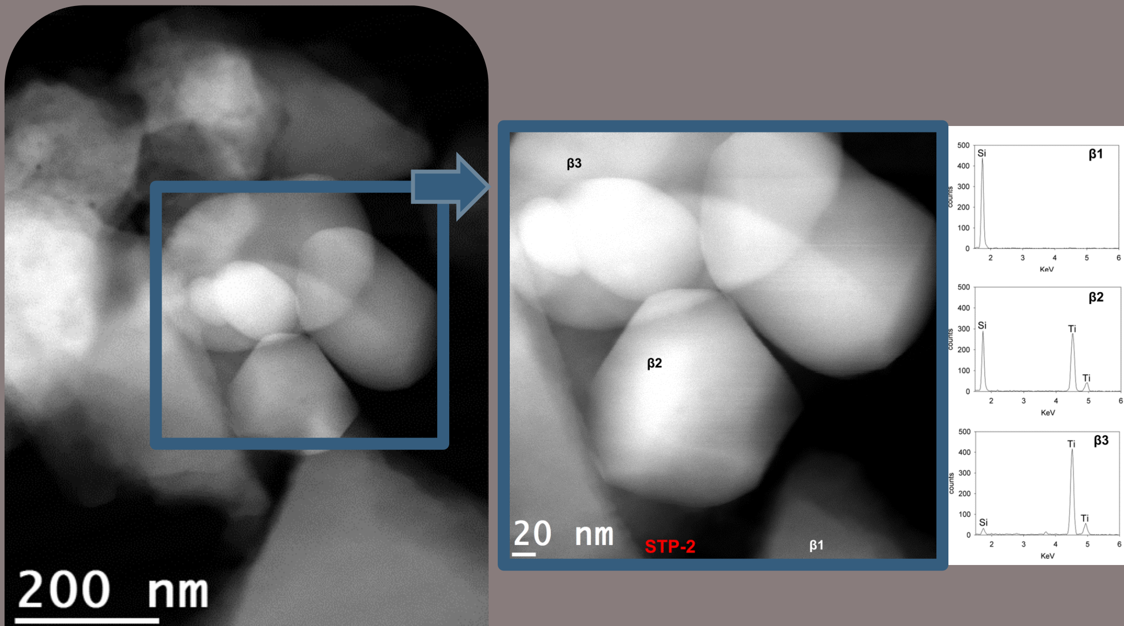
- Si is clearly detected but Ti peaks are not detected on the three spots

Due to:

the homogeneous distribution of Ti in atomic level and the low concentration of Ti

Results of nano-materials' characterization

STEM-HAADF



➢It does show a visible contrast between the particles and matrix

✓Zones with higher contrast correspond to TiO_2 particles, where Ti has higher atomic number than Si in silica matrix

✓Independent TiO_2 domains

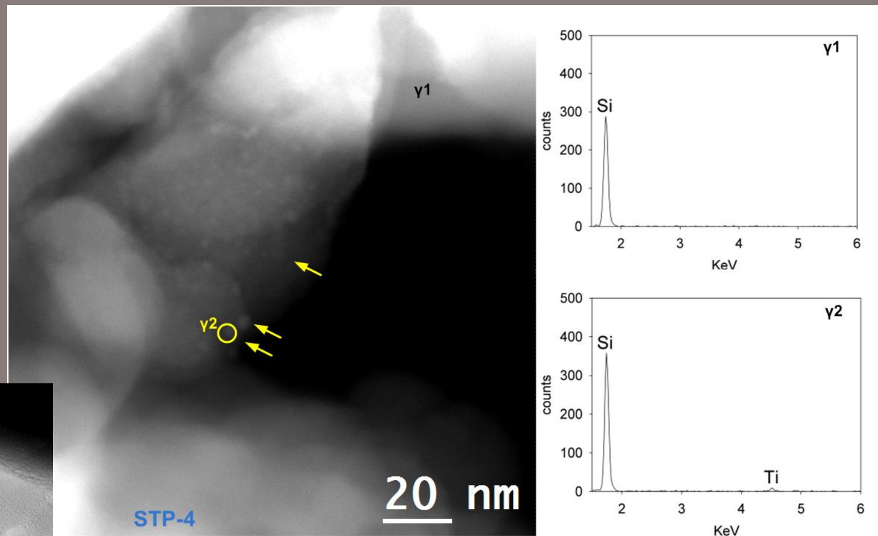
X-EDS spectra

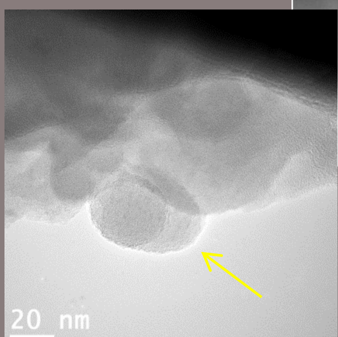
β1 spot (lower intensity) ➡ Ti is not detected

β2 and β3 spots (higher contrast zones) ➡

1. Ti peaks
2. β3 >> β2 (higher Ti peaks)

Results of nano-materials' characterization





STEM-HAADF

➢It does show a visible contrast between the particles and matrix

Smaller and spherical TiO_2 nanoparticles as TEM

X-EDS spectra

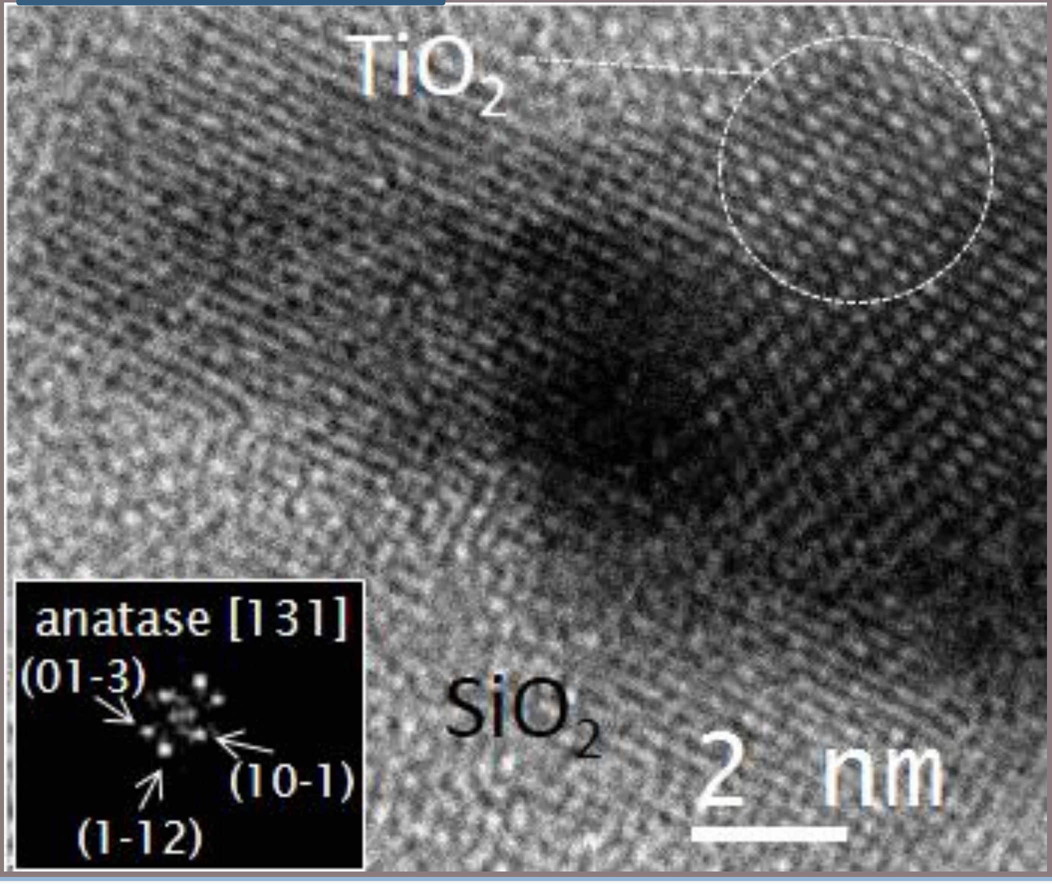
γ1 spot (lower intensity) ➡ Ti is not detected

γ2 spot (higher contrast zone) ➡ Ti is detected

Results of nano-materials' characterization

HREM

STP-2/STP-4



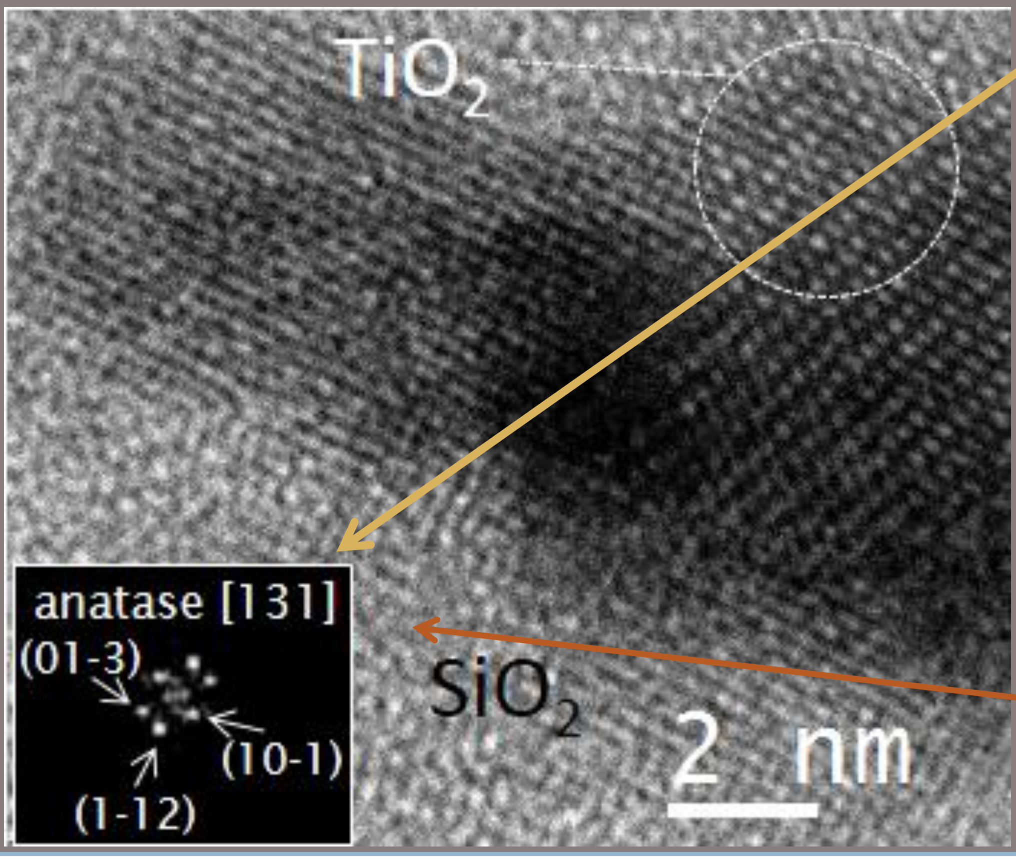
Further insights into the structure of the nanocomposites

- ✓TiO_2 in separate domain inside the silica matrix
- ✓The darker zones could correspond to the overlapping of at least two crystalline particles
- ✓Observation of TiO_2 nanoparticles is difficult because they are embedded within the silica matrix

Results of nano-materials’ characterization

HREM

STP-2/STP-4



Digital Diffraction Patterns with application of Fourier Transformation to the visible lattice spacing in the crystalline structure of the materials

ANATASE TiO_2

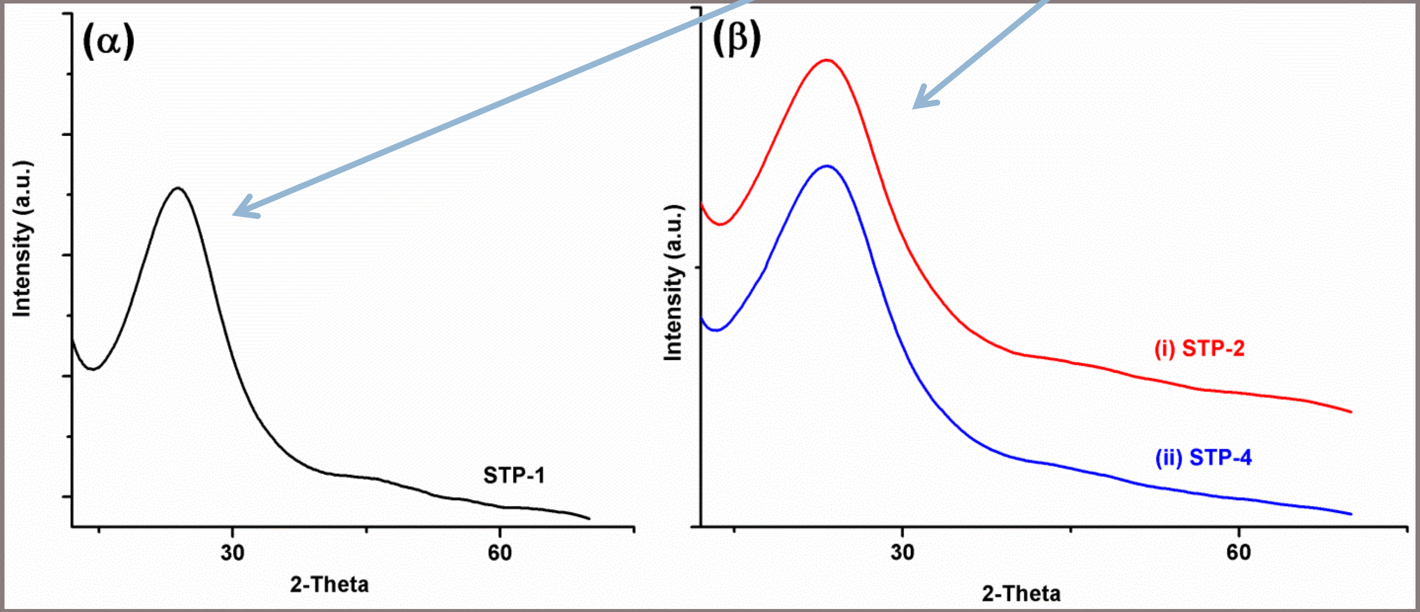
Formation of anatase TiO_2 inside the silica matrix through the hydrolysis of Ti and Si alkoxides at room temperature

Silica matrix is an amorphous phase

Results of nano-materials' characterization

X-Ray Diffraction

Amorphous SiO_2



➢No diffraction peaks corresponding to TiO_2 crystalline phases (anatase, rutile or brookite) but this is in accordance with previous published results

➢Small size and the lack of orientation observed in the crystalline network ⇒ responsible for the absence of XRD crystalline peaks

Results of nano-materials' characterization

Comparison results of adsorption/desorption N_2 and TEM

Draw significant conclusions about texture and the microstructure

1. Formation of **anatase crystals** at **ambient temperature**

Due to the peptization process occurring during syntheses in the presence of Oxalic acid

According to published results the addition of acid facilitates the growth of anatase from the amorphous phase

STP-1

Both the fast hetero-condensation and the low Ox concentration restrict the peptization process

STP-2 and STP-4

Amorphous phase is first created. Peptization process occurs during the magnetic stirring (24h) in the presence of Ox which promotes the formation of anatase crystals observed by HREM

Results of nano-materials' characterization

Comparison results of adsorption/desorption N_2 and TEM

Draw significant conclusions about texture and the microstructure

2. Larger size of TiO_2 nano-particles and aggregates in STP-2

Explanation of reduced pore volume and subsequent low surfaces area observed by adsorption/desorption N_2

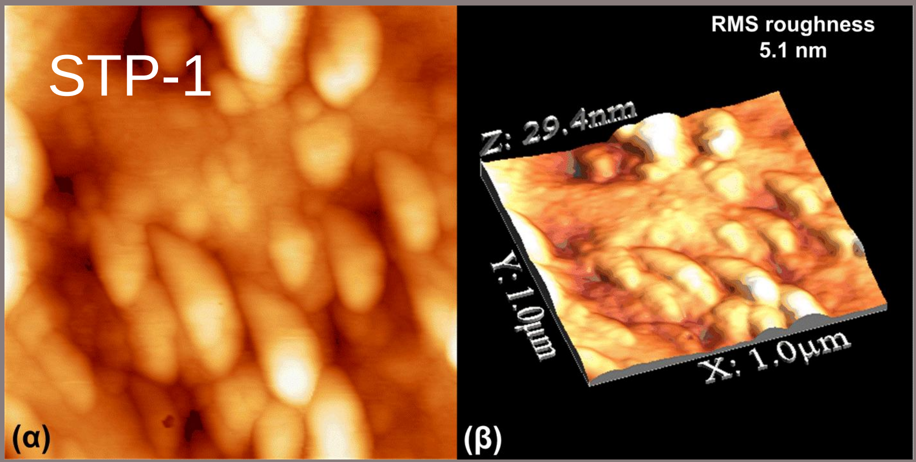
STP-2

High aggregation of TiO_2 crystalline particles, which does not contain pores, produce dramatic decrease in the pore volume and surface area

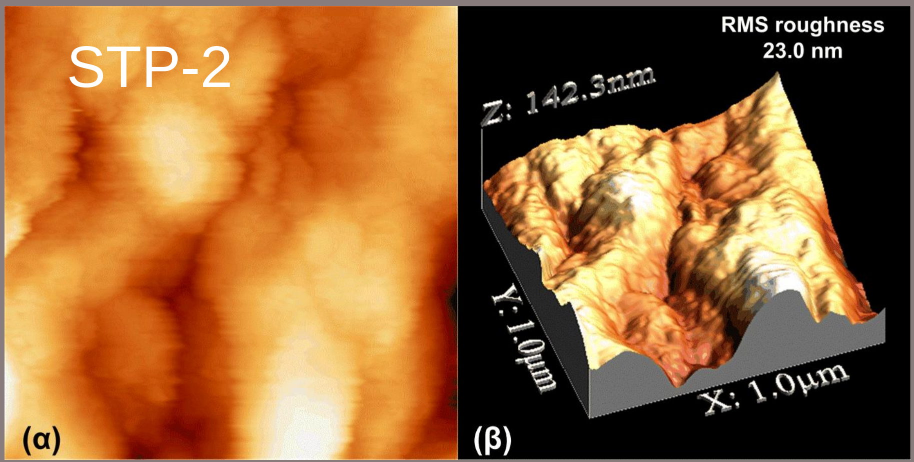
These evidences are in accordance with other published results, where nanocomposites containing non-pores SiO_2 particles exhibit decreased pore volume

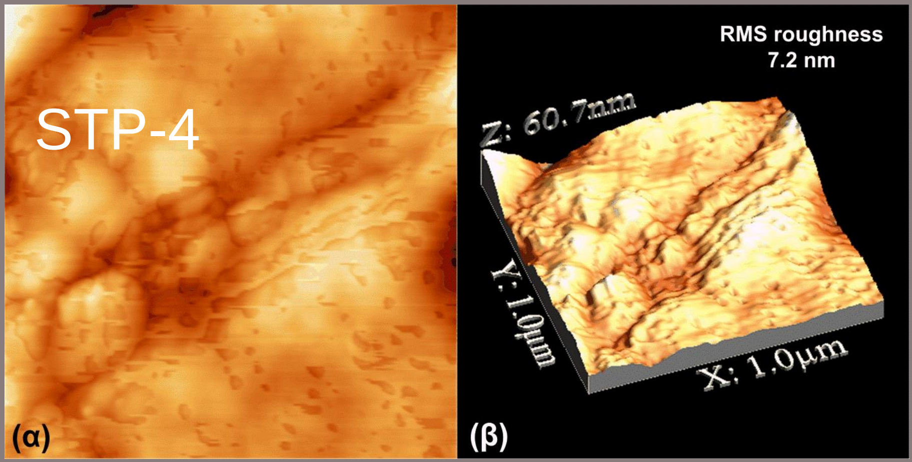
Results of nano-materials' characterization

AFM (2D and 3D)



All materials consist of aggregates with morphology similar to that observed by TEM



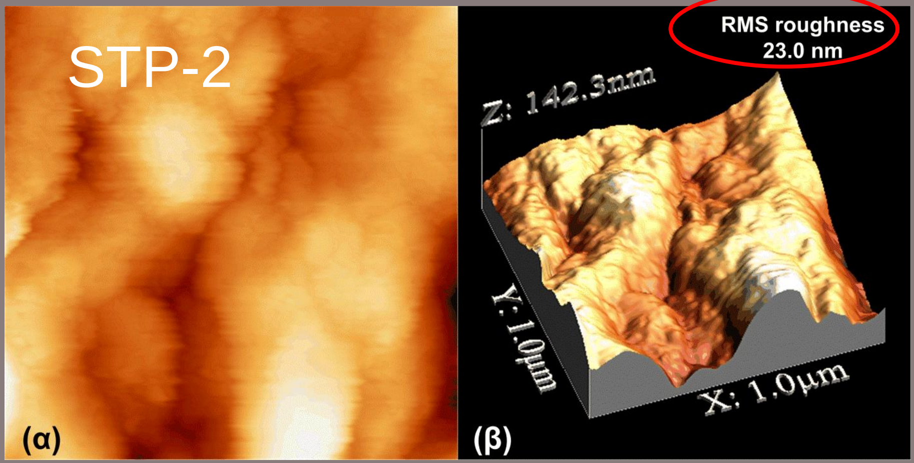


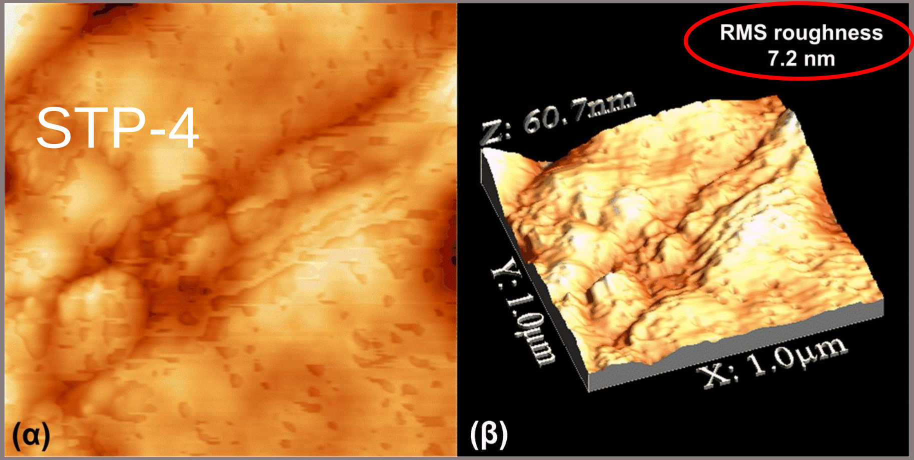
Roughness peaks due to the presence of the organic component (PDMS). Elastic behavior of PDMS chains, which shrink greatly during the drying process of the gel network

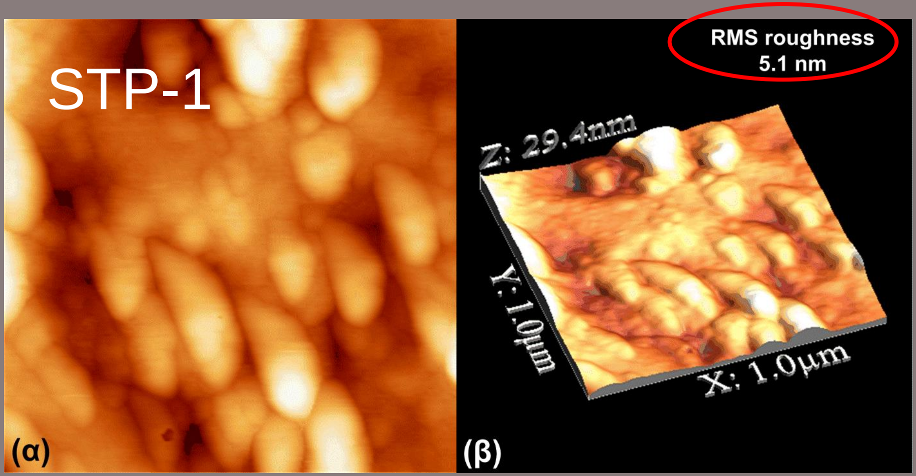
Results of nano-materials' characterization

AFM (2D and 3D)

LT







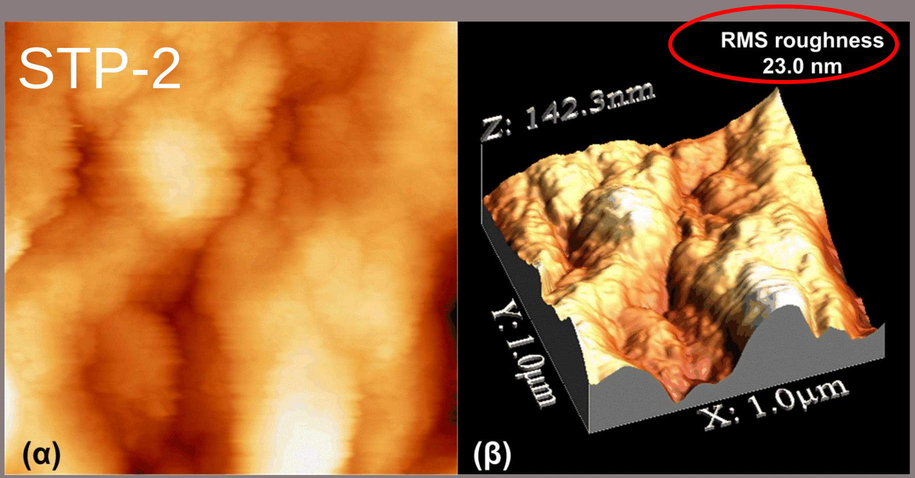
STP-2/STP-4 with higher content of Ox present higher roughness values than STP-1

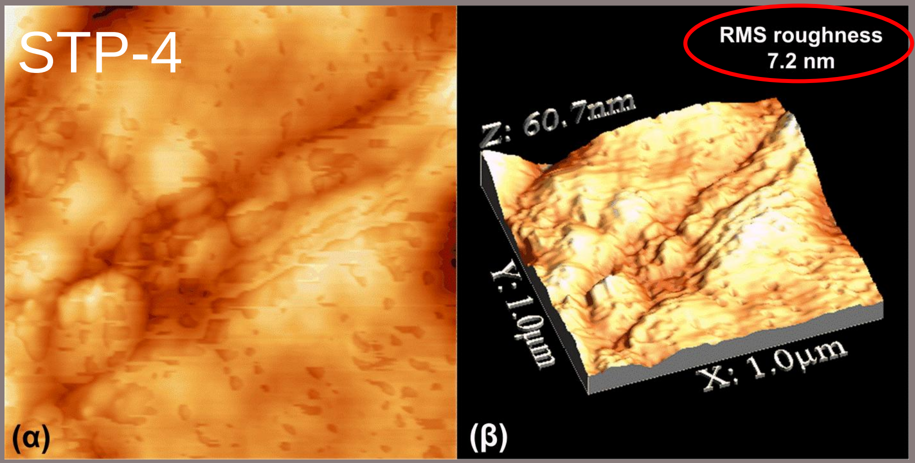
TiO_2 nanoparticles inside the SiO_2 matrix

These evidences are in accordance with other published results.

Results of nano-materials' characterization

AFM (2D and 3D)





STP-4 with higher content of Ox produces a surface of much lower roughness value (7.2 nm)

but

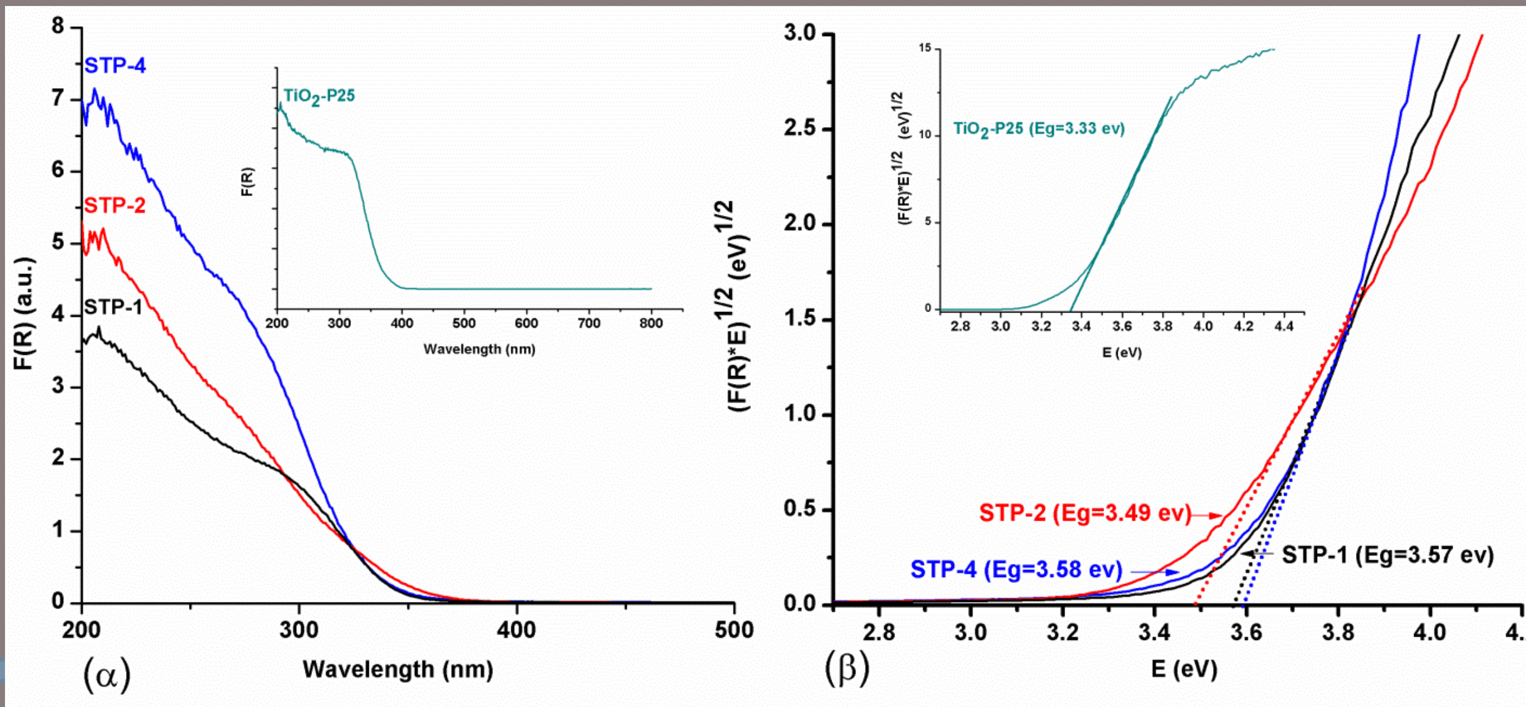
STP-2 with medium content of Ox produces a surface of the highest roughness value (23.0 nm)

due to the formation of larger size of TiO_2 and the presence of their aggregates

Results of nano-materials' characterization

UV-Vis DRS

Equation Kubelka-Munk
$F(R)=(1-R)^2/2R$

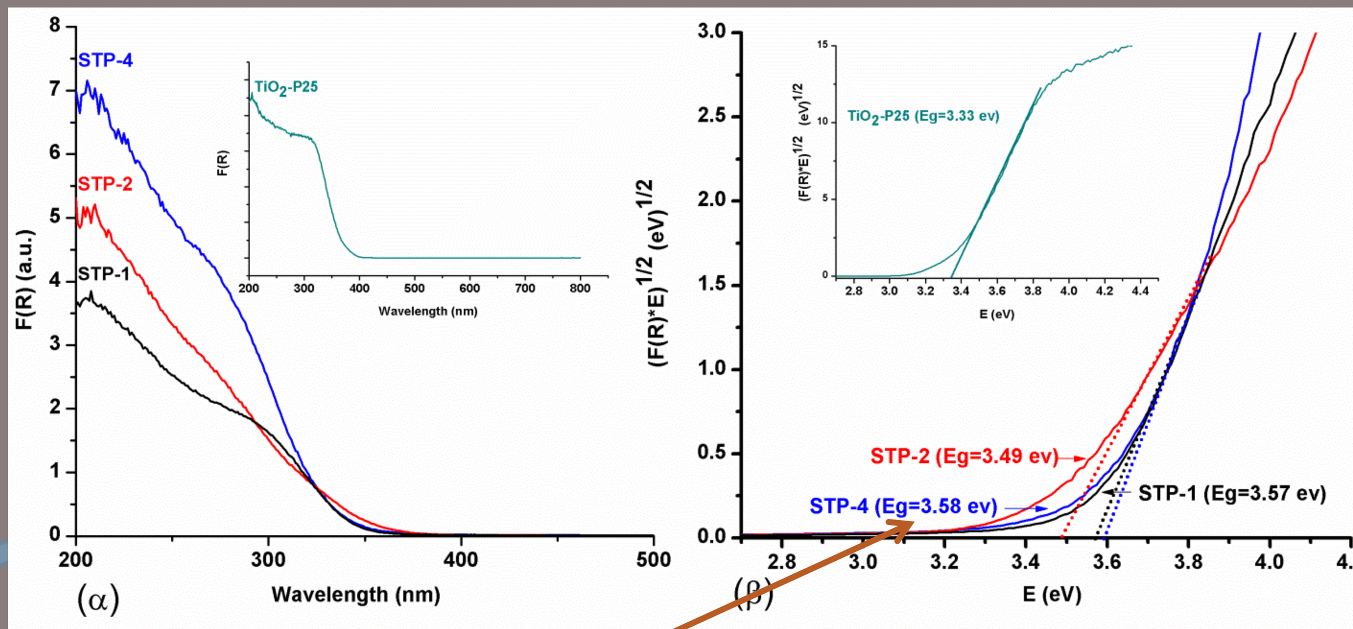


➢SiO_2 does not absorb in the range 200-800 nm
➢Eg of P25 lower than nanomaterials, where the TiO_2 are embedded in the SiO_2 matrix

Results of nano-materials' characterization

UV-Vis DRS

Equation Kubelka-Munk
$F(R)=(1-R)^2 /2R$

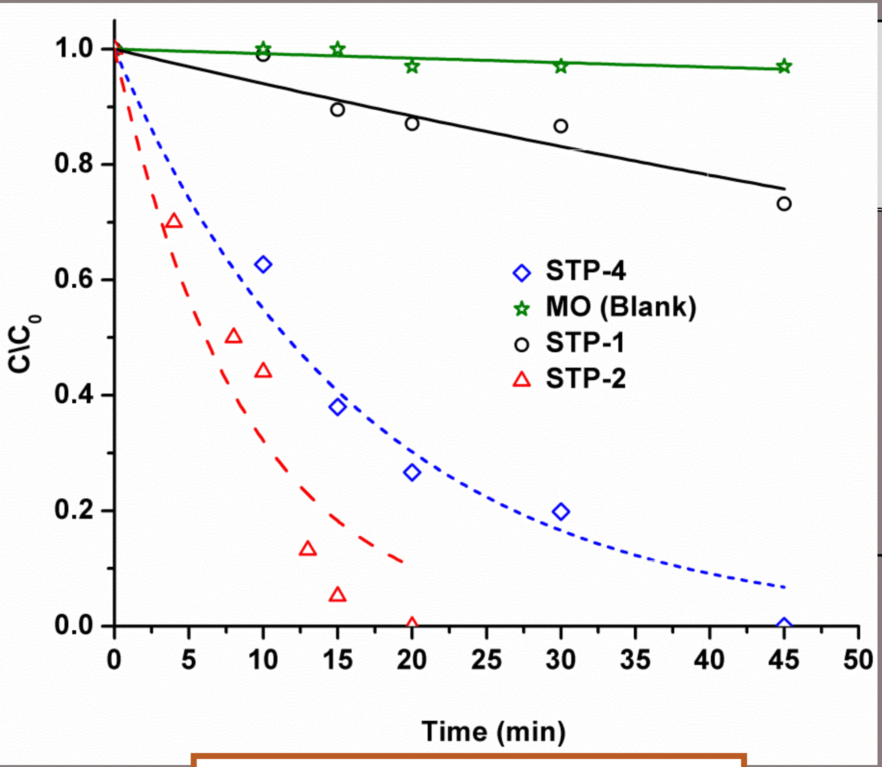


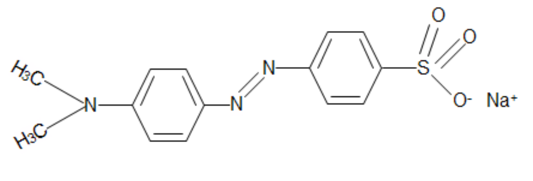
✓STP-2 shows the lowest Eg value
Quantum Size Effect: the Band gap reduced as the particle size increased

✓STP-1 ≈ STP-4
Even though that separate domains in STP-1 have not detected there is material that absorbed in this range

Results of nano-materials’ characterization

Photocatalytic activity





Πορτοκαλί του μεθυλίου
(*Methyl Orange, MO*)

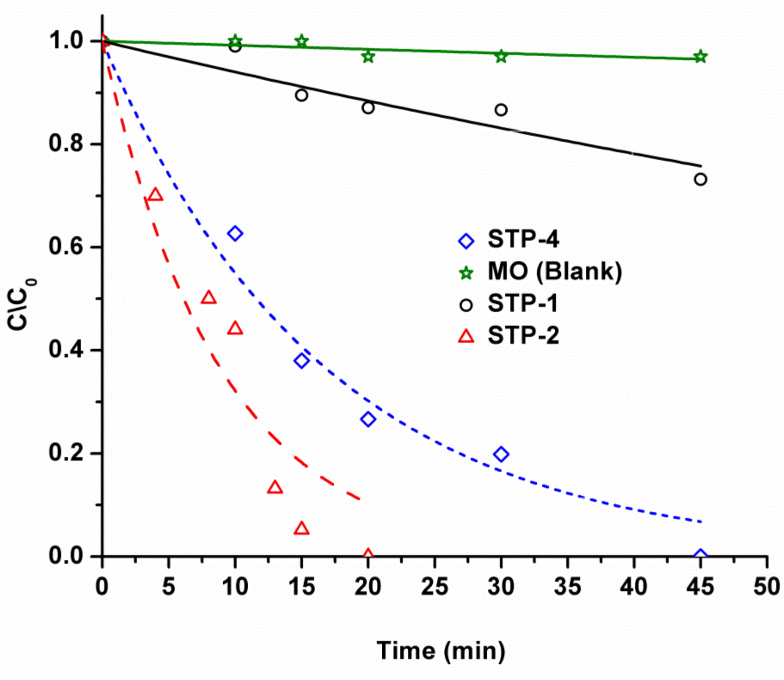
Pseudo-first kinetic rate

Nanomaterial	k (10^{-3} min^{-1})	r^2
MO (blank)	0.8	0.91
STP-1	6	0.90
STP-2	113	0.94
STP-4	60	0.98

✓Photochemical degradation of MO is negligible
✓STP-1 lower activity than STP-2 and STP-4

Results of nano-materials' characterization

Photocatalytic activity



Pseudo-first kinetic rate

Nanomaterial	k (10^{-3} min^{-1})	r^2
MO (blank)	0.8	0.91
STP-1	6	0.90
STP-2	113	0.94
STP-4	60	0.98

✓STP-2 > STP4

STP-2: larger size of TiO_2 according TEM and DRS

BUT

it contains higher content of separate domains

According to published results, TiO_2 nanoparticles with similar size (as STP-2) 6-7 nm show enchanced photocatalytic properties.

Results of nano-materials' characterization

Photocatalytic activity

Ox as hole-scavenger

- Oxalic ions are good bidentate ligands and at low pH values absorbed strongly on TiO_2 surface
- Oxalic ions' ability to produce $CO_2^{\cdot -}$ through their reaction with h^+ according to:

$$C_2O_4^{2-} + h^+ \rightarrow CO_2 + CO_2^{\cdot -}$$

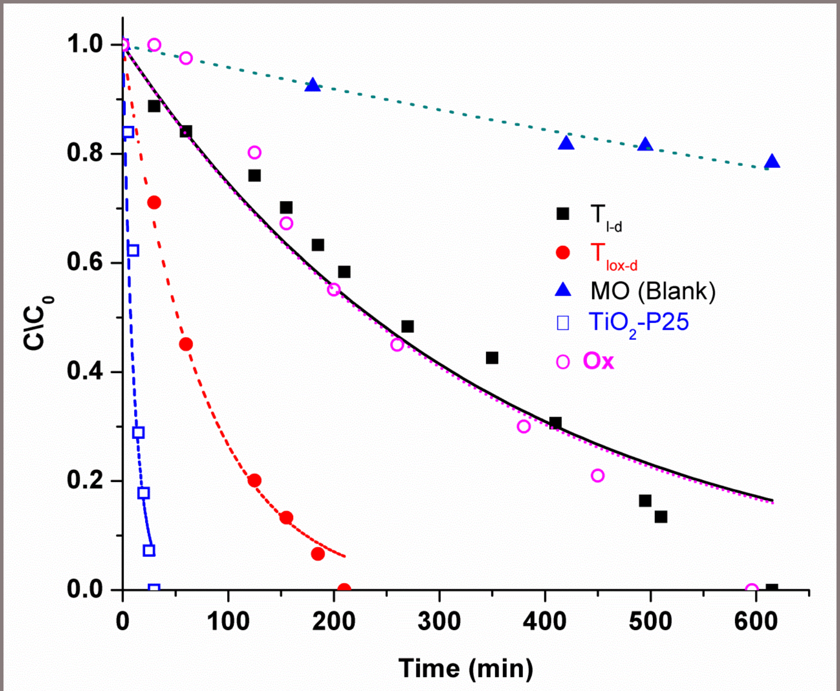
h^+ capturing from Ox restrict the recombination of e^- and h^+

$CO_2^{\cdot -}$ either direct decomposes the MO or reacts with O_2 producing $O_2^{\cdot -}$ / $HO_2^{\cdot}$

Published studies show the efficiency of EDTA (another good bidentate ligand) as hole-scavenger in MO degradation

Results of nano-materials' characterization

Photocatalytic activity



TiO_2 Formulations	k (10^{-3} min^{-1})	r^2
TiO_2-P25	73	0.93
T_{lox}-d	13	0.99
Ox	2.9	0.94
T_l-d	2.9	0.95
MO (blank)	0.4	0.98

✓Crystalline TiO2-P25 (70% anatase and 30% rutile) highest photocatalytic activity

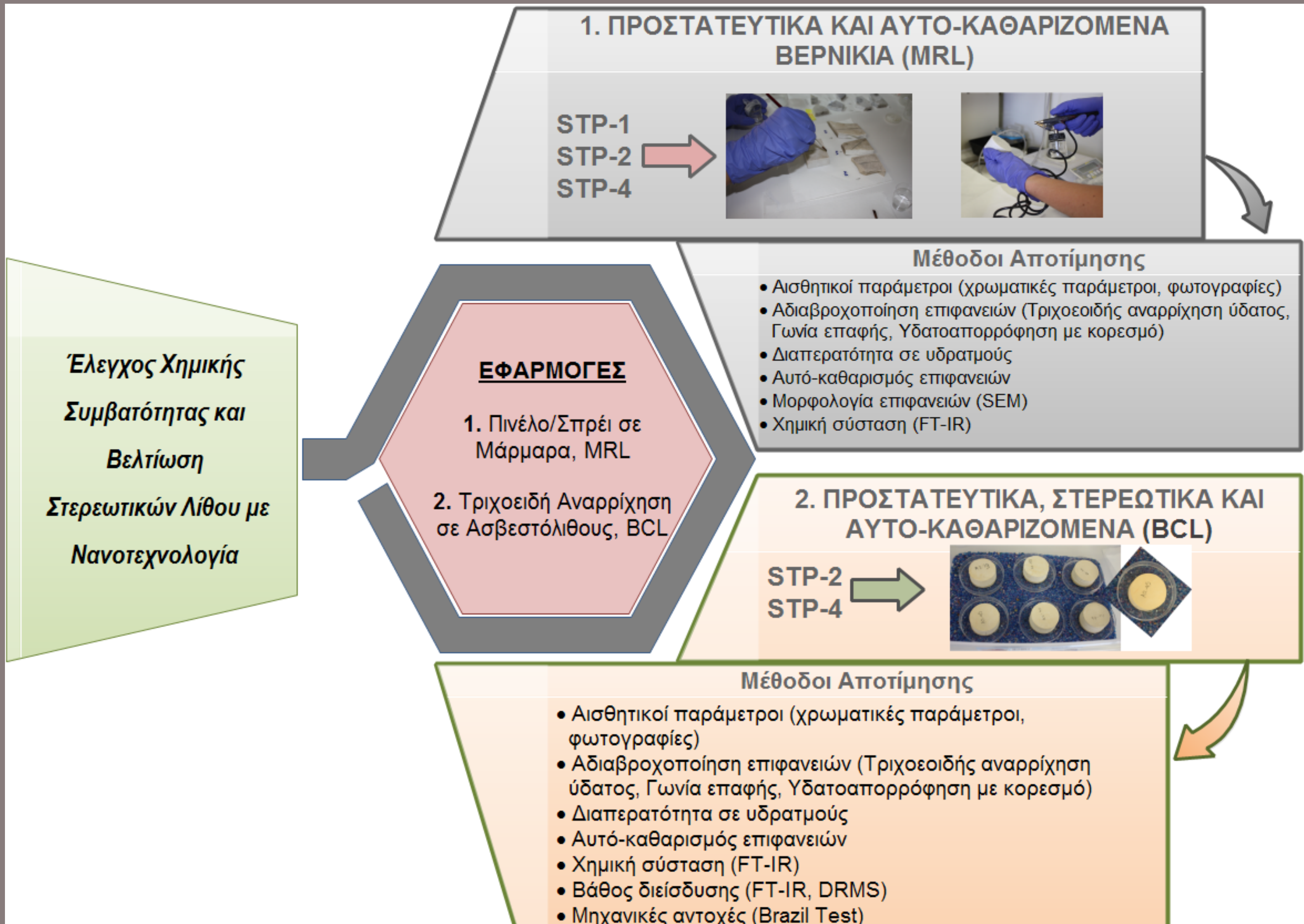
✓Oxalic acid improves the photocatalytic activity of TiO_2

BUT STP-2:
lower Ox concentration than STP-4
TiO_2 nanoparticles

Results of nanomaterials' application

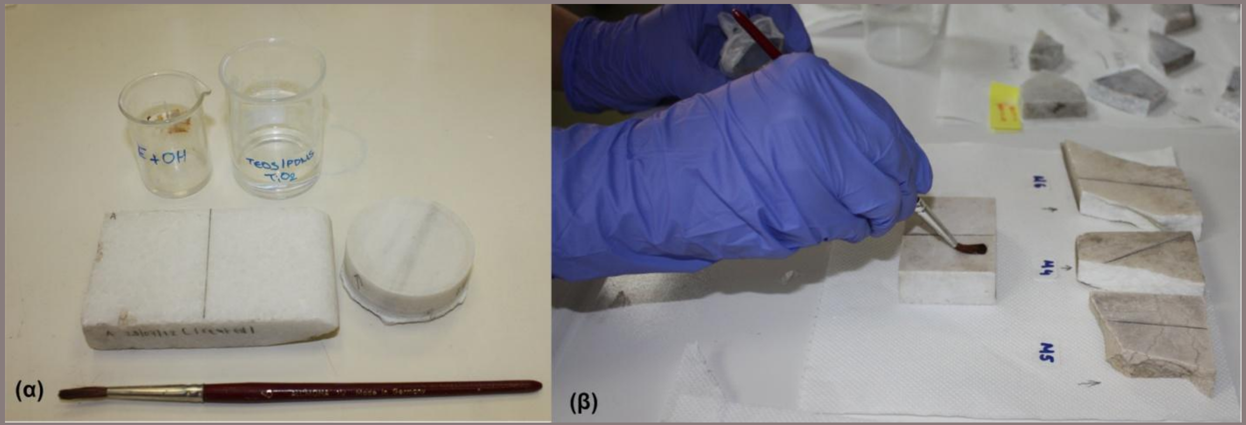
Part B

Application of the nanocomposites on stones



Application of the nanocomposites on stones

Coating on marbles



STP-1: Dionysos and Thasos
STP-2 and STP-4: Naxos

Application of the nanocomposites on stones

Consolidant on limestones

Consolidation and self-cleaning properties

<u>STP-2 and STP-4:</u>
Limestone (Alfas, Rethymno, Crete)

Διαμορφωμένα δοκίμια ασβεστιτικών δοκιμίων

Effectiveness of the nanocomposites as coating on marbles

- Dry matter

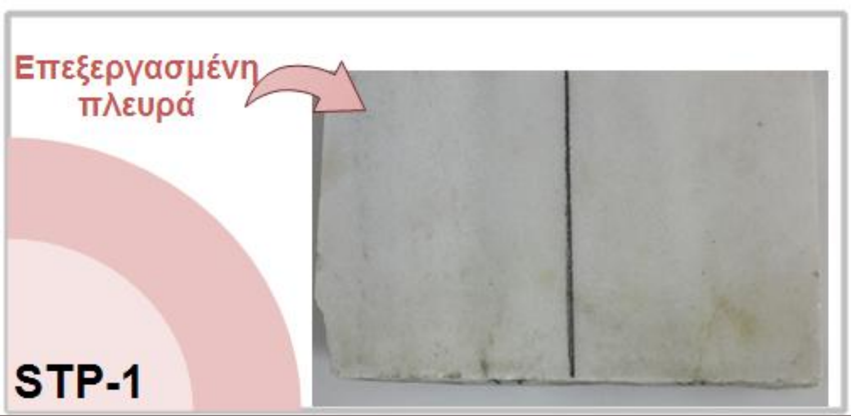
Treated	Dry matter ($mg \cdot cm^{-2}$)
STP-1	0.658±0.138
STP-2	0.412±0.011
STP-4	0.424 ±0.042

Two applications (due to lower photocatalytic activity)

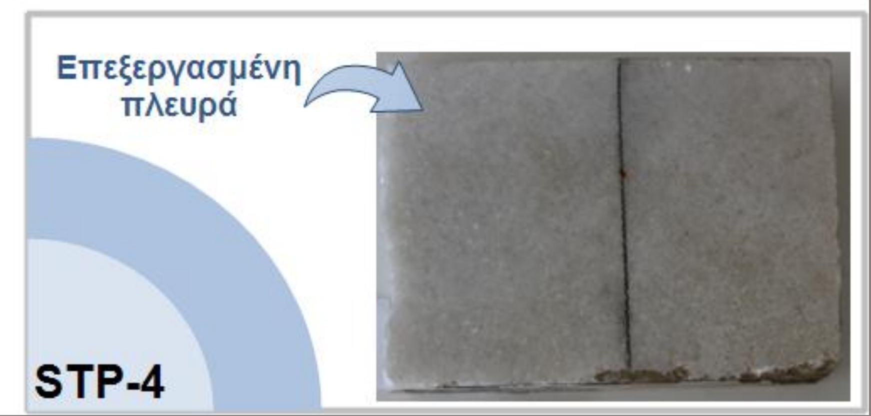
Effectiveness of the nanocomposites as coatings on marbles

- Color alteration

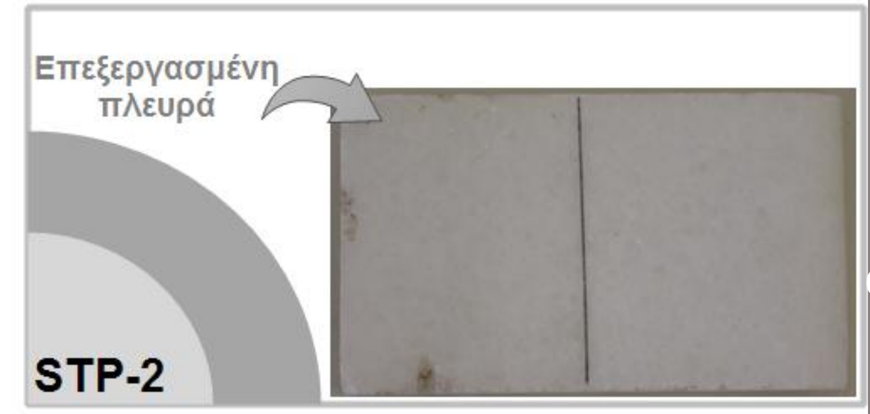
$\Delta E^* = 3.14 \pm 0.36$



$\Delta E^* = 1.88 \pm 0.05$



$\Delta E^* = 0.61 \pm 0.05$



$\Delta E^* = 2\text{-}3$
Cannot be detected by naked eye

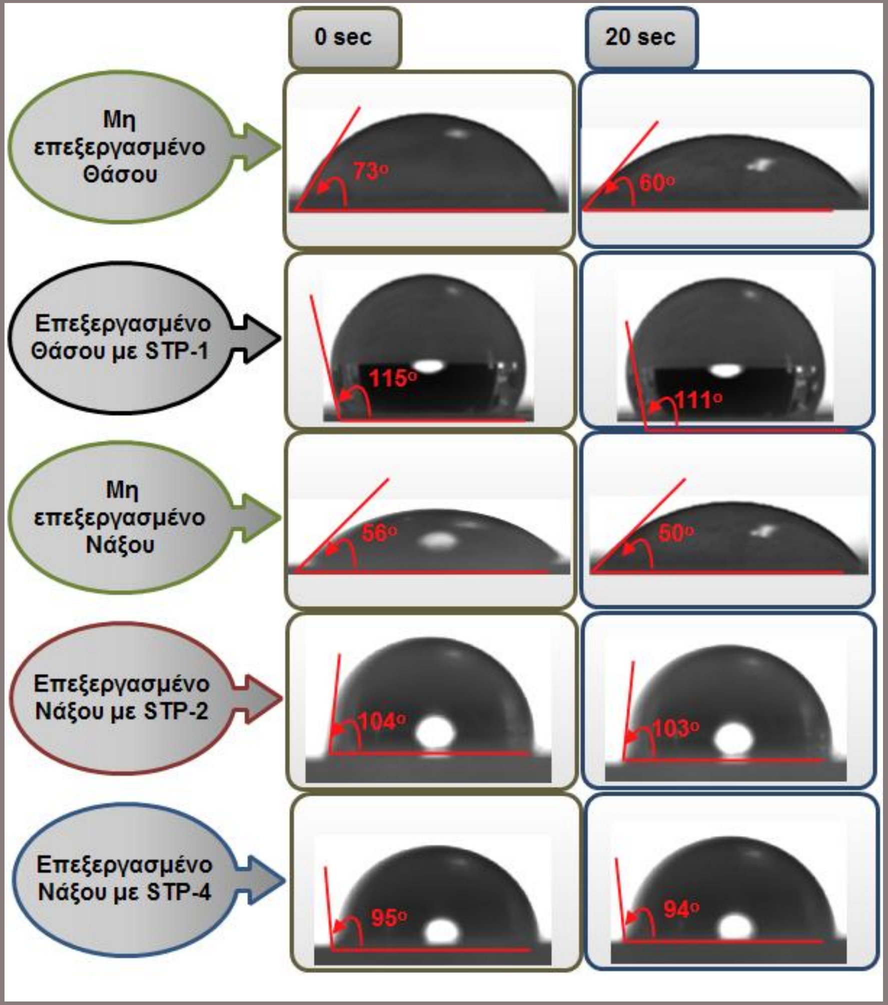
- Dispersions of colloidal solution of commercial TiO_2 due to its white color induced chromatic variations ΔE* higher than 3

Effectiveness of the nanocomposites as coating on marbles

➢Hydrophobic effectiveness

Static Contact angle

Treated surfaces: CA> 90º (hydrophobic character)



Effectiveness of the nanocomposites as coating on marbles

➢Hydrophobic effectiveness

Static Contact angle

		Untreated	Treated STP-1	Treated STP-2	Treated STP-4	% Change		
						STP-1	STP-2	STP-4
Contact angle, CA (°)	0 sec	56.2 ±3.0	-	104.3 ±2.0	95.4 ± 2.2	-	+86	+70
	20 sec	50.0±2.8	-	103.2±1.2	93.6± 1.6	-	+106	+87
	0 sec	72.6 ±3.0	114.8±0.4	-	-	+58	-	-
	20 sec	59.9±2.7	111.3±0.8			+86		

➢**Hydrophobicity due to the presence of PMDS (same content in all the nanocomposites)**

PDMS **reduces** the **surface energy** of the materials and **increases the roughness (high values of shrinkage)**

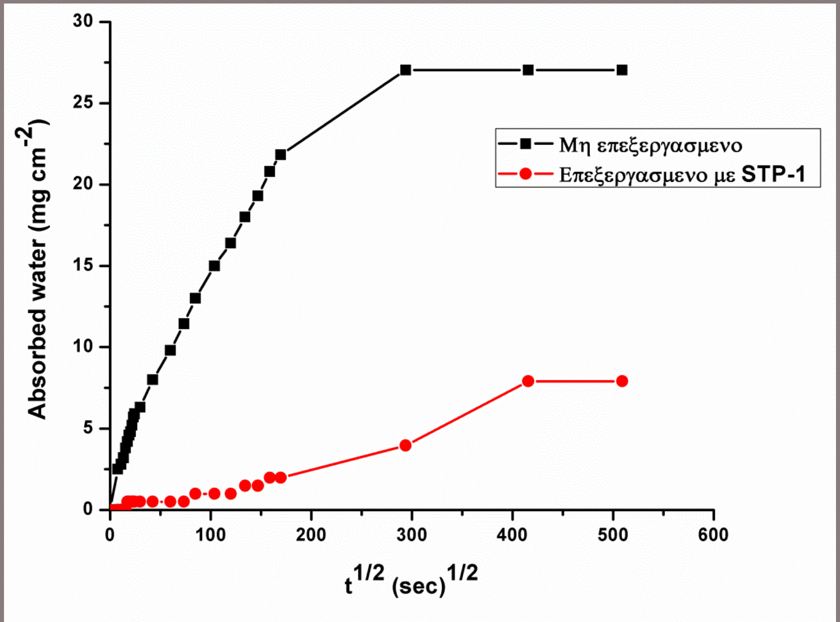
➢**STP-2>STP-4 due to the higher roughness values according to** AFM

Effectiveness of the nanocomposites as coating on marbles

➢Hydrophobic effectiveness

Water Capillary absorption

	% Change	
	WCA	TWCA
STP-1	-88	-41
STP-2	-88	-47
STP-4	-80	-37



Effectiveness of the nanocomposites as coating on marbles

➢ Water vapor permeability

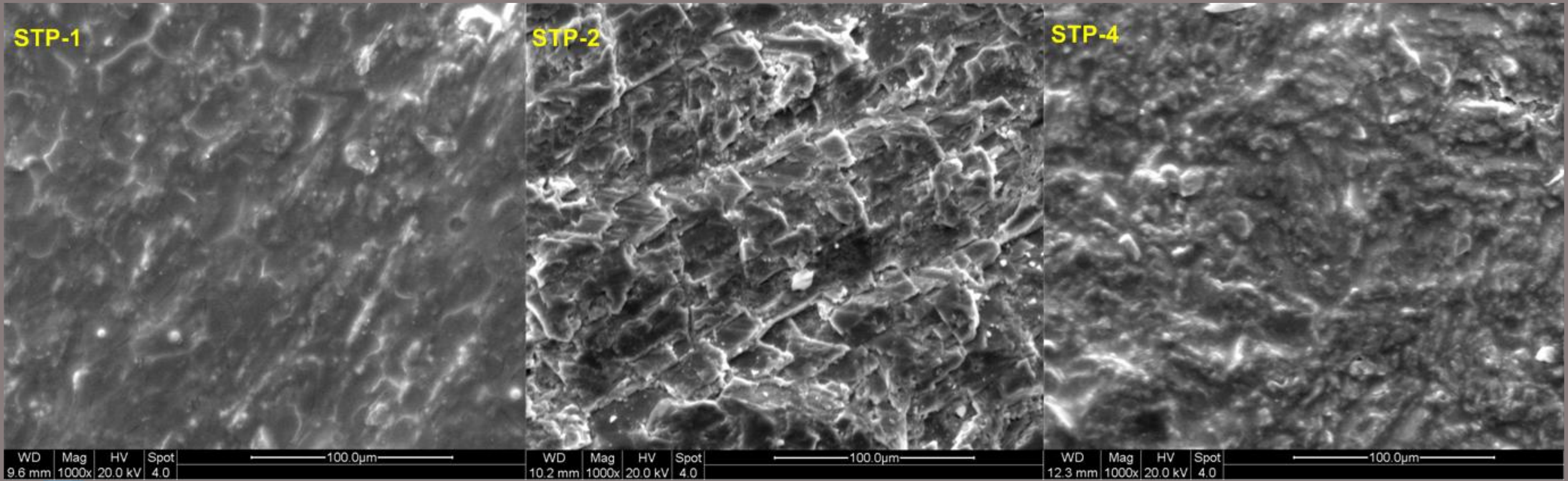
	% Change (WVP)
STP-1	-34
STP-2	-17
STP-4	-22

Within the acceptable ranges of the hydrophobic materials (reduction up to 35%)

Chemical compatibility

Effectiveness of the nanocomposites as coating

Treated surfaces of marbles (SEM)



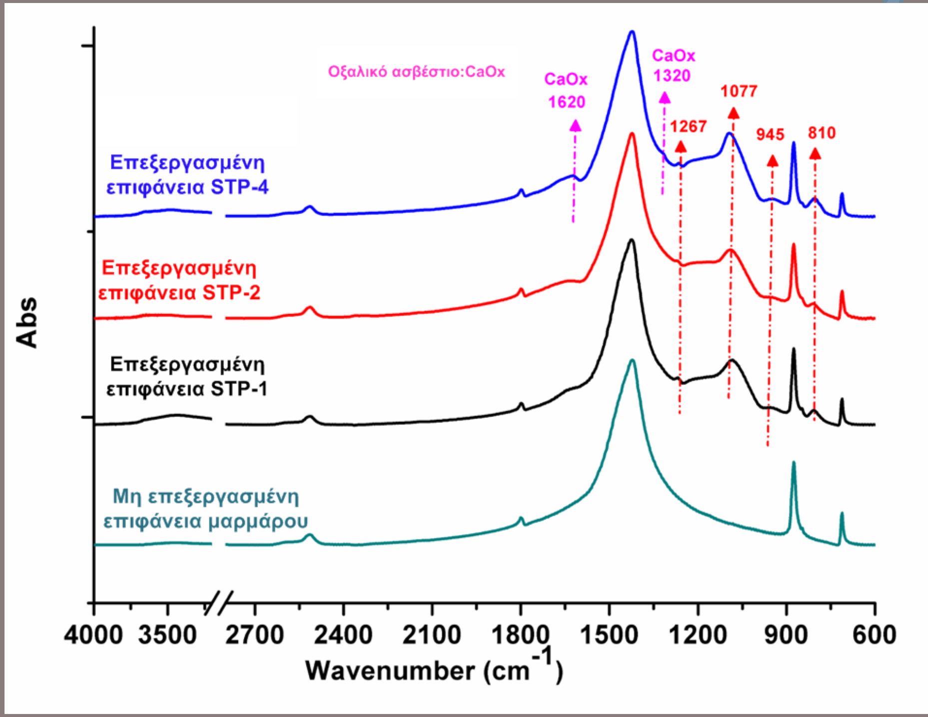
➢Chemical compatibility

➢Crack-free treated surfaces

This cohesive structure of the nanomaterials was achieved due to Ox and PDMS

Effectiveness of the nanocomposites as coating

Treated surfaces of marbles (FT-IR)



- 1267 cm^{-1}
  copolymerization of PDMS and TEOS
- 1077 and 810 cm^{-1}
  neo-formed Si-O-Si bonds
- 945 cm-1
  neo-formed Si-O-Si bonds and Si-OH
- 1620 and 1320 cm^{-1}
  STP-4 due to Calcium Oxalate (CaOx)

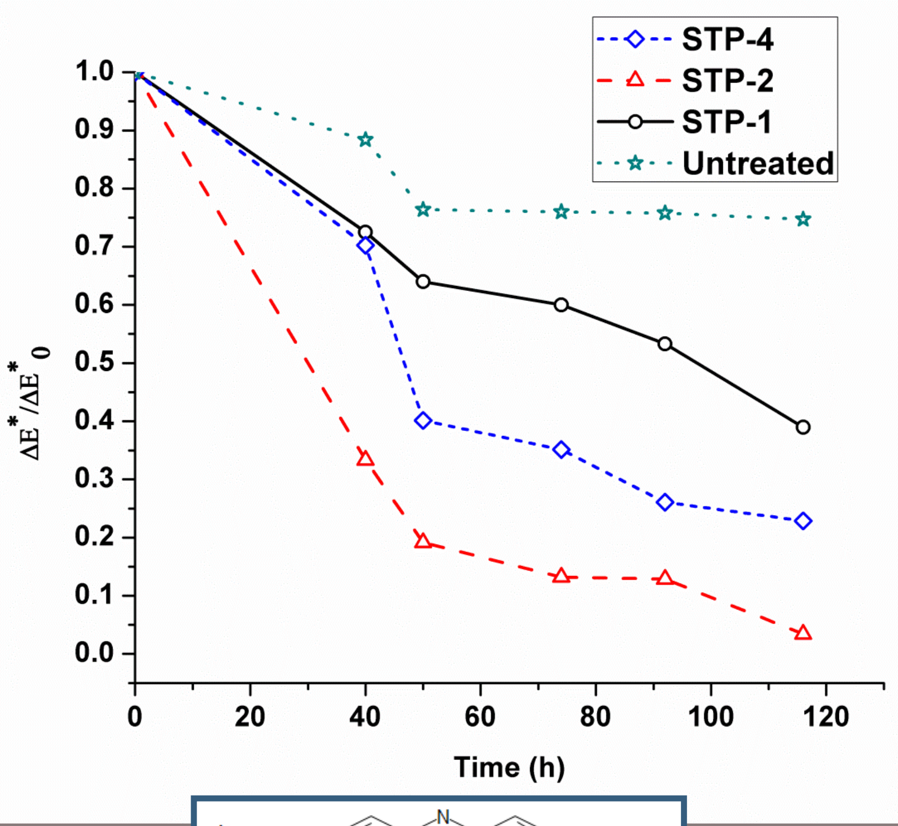
CaOx has been identified into well-preserved layers-patinas on monument surfaces

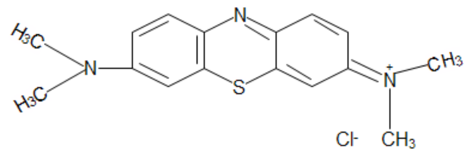
Chemical compatibility

CaOx
1. is more stable than $CaCO_3$
2. It can act protectively against the weathering deterioration

Effectiveness of the nanocomposites as coating

Self-cleaning marbles





Μπλε του μεθυλενίου
(*Methylene Blue , MB*)

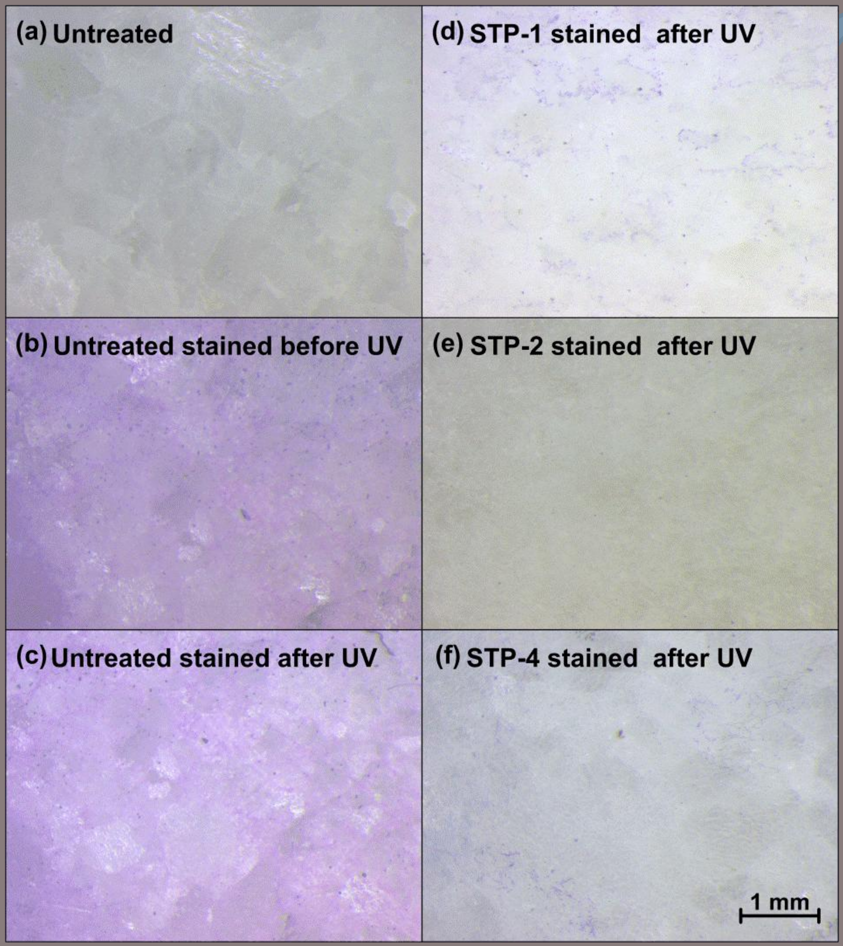
➢The results match perfectly with those obtained from the photocatalytic tests of the nanocophosites

STP-2>STP-4>STP-1

•STP-1 lowest activity due to absence of separate TiO_2 domains
•STP-2 higher activity than STP-4 due to the presence of greater amount of crystals as observed by TEM

Effectiveness of the nanocomposites as coating

Self-cleaning marbles

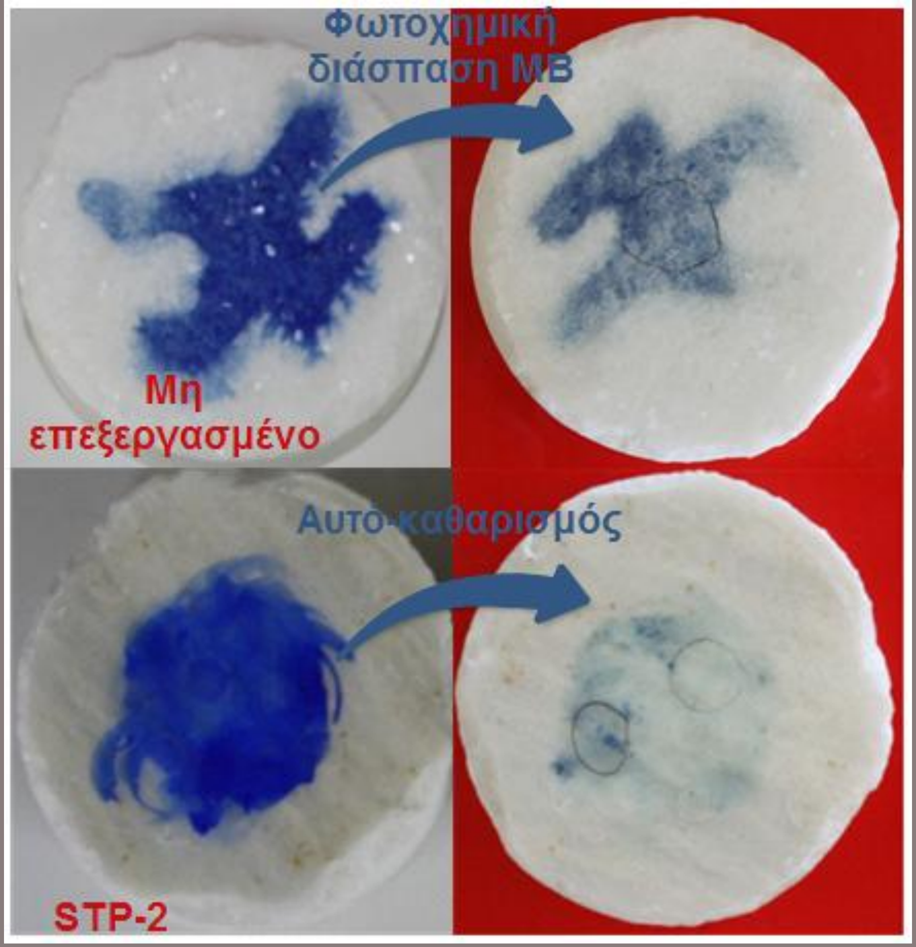


Optical Microscopy
Before and after 116 h UV irradiation

➢ These results confirm that STP-2 presents the better photocatalytic behavior.
The most effective color removal has been observed on the marble treated with STP-2

Effectiveness of the nanocomposites as coating

Self-cleaning of fresh marbles



Effectiveness of the nanocomposites as coating

Self-cleaning marbles

Effectiveness of the nanocomposites as consolidant on limestone

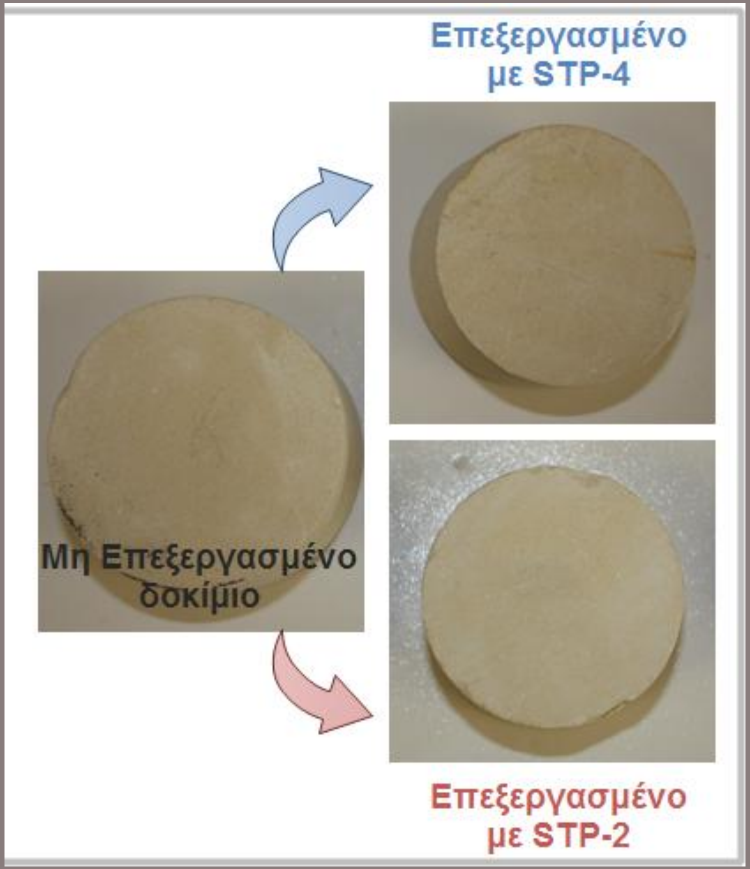
- Dry matter

	Dry matter	
	% w/w	$g \cdot cm^{-2}$
STP-2	2.21 (±0.17)	0.112 (± 0.007)
STP-4	1.96 (±0.19)	0.097 (± 0.009)

⇨ The absorbed quantity of the product is of the same level

Effectiveness of the nanocomposites as consolidant on limestone

➢ Color alteration



	STP-2	STP-4
ΔE*	0.89(±0.05)	0.65(±0.03)

ΔE^* = 2-3
Cannot be detected by naked eye

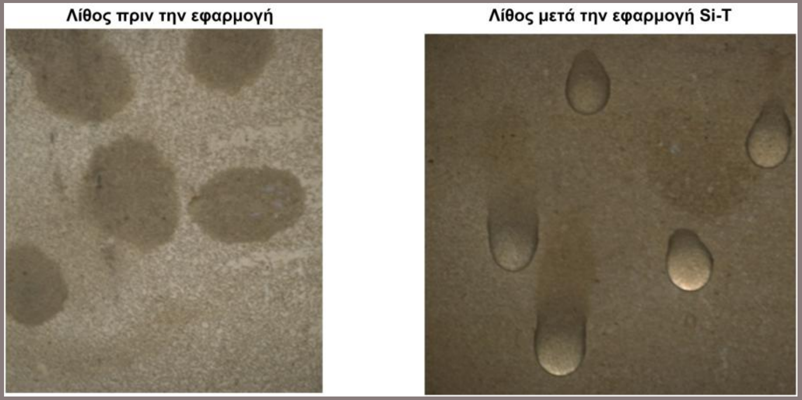
Effectiveness of the nanocomposites as consolidant on limestone

➢Hydrophobic effectiveness

Static Contact angle

➢Hydrophobicity due to the presence of PMDS (same content in all the nanocomposites)
PDMS **reduces** the **surface tension** of the materials and **increases the roughness (high values of shrinkage)**

➢**Drop of water is maintained by 1200 sec**



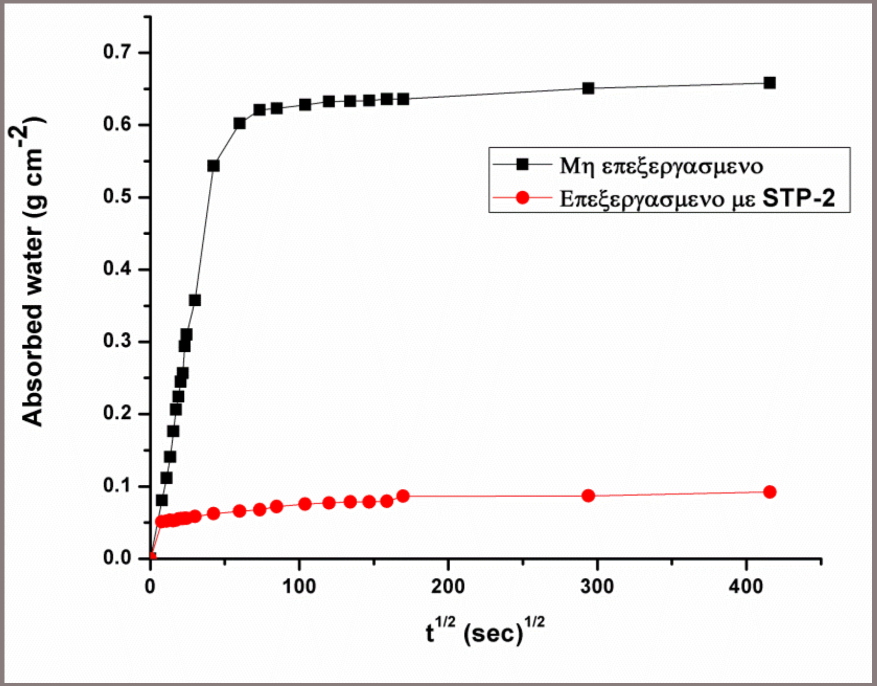
Effectiveness of the nanocomposites as consolidant on limestone

➢Hydrophobic effectiveness

Water Capillary absorption and Water Saturation

	% Change		
	WCA	TWCA	Saturation
STP-2	-95	-77	-31
STP-4	-97	-83	-27

✓Hydrophobic character (Presence of PDMS)



Effectiveness of the nanocomposites as consolidant on limestone

- Water vapor permeability

	Untreated	Treated STP-2	Treated STP-4
WVP (g $cm^{-2} \cdot h^{-1}$)	0.0011 (±0.0001)	0.0010 (±0.0001)	0.0010(±0.0001)

-9%

Chemical compatibility

Within the acceptable ranges of the hydrophobic materials (reduction up to 35%)

Effectiveness of the nanocomposites as consolidant on limestone

➢Mechanical properties (Brazilian test)

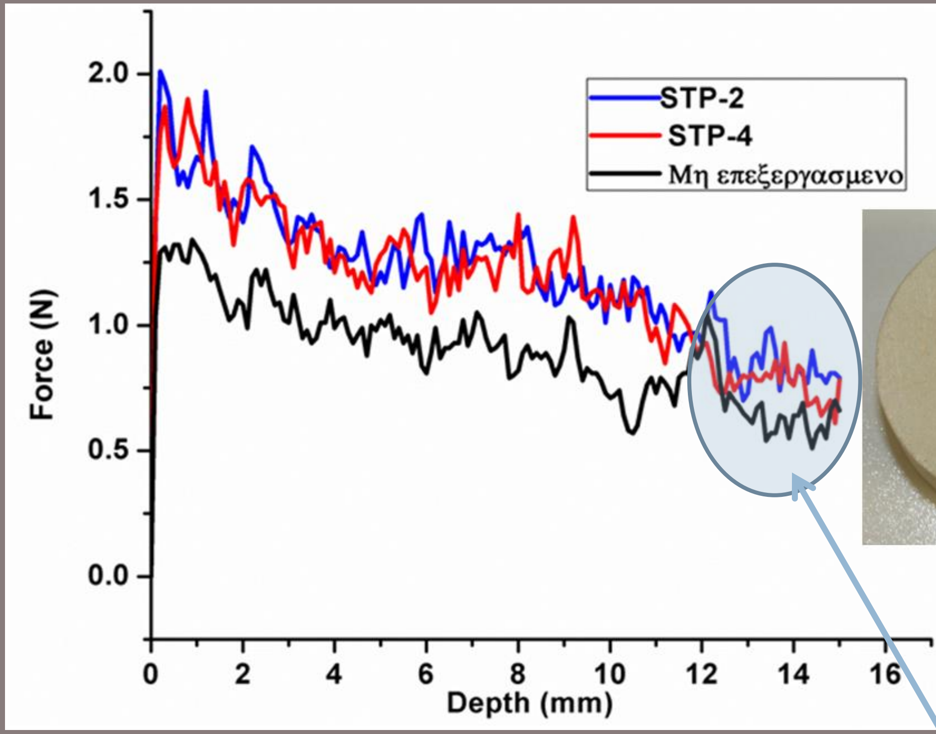
	Untreated	Treated STP-2	Treated STP-4
Tensile strength (MPa)	2.81 (±0.12)	3.43 (±0.58)	3.44 (±0.38)

+22%

Providing a considerable consolidation effect

Effectiveness of the nanocomposites as consolidant on limestone

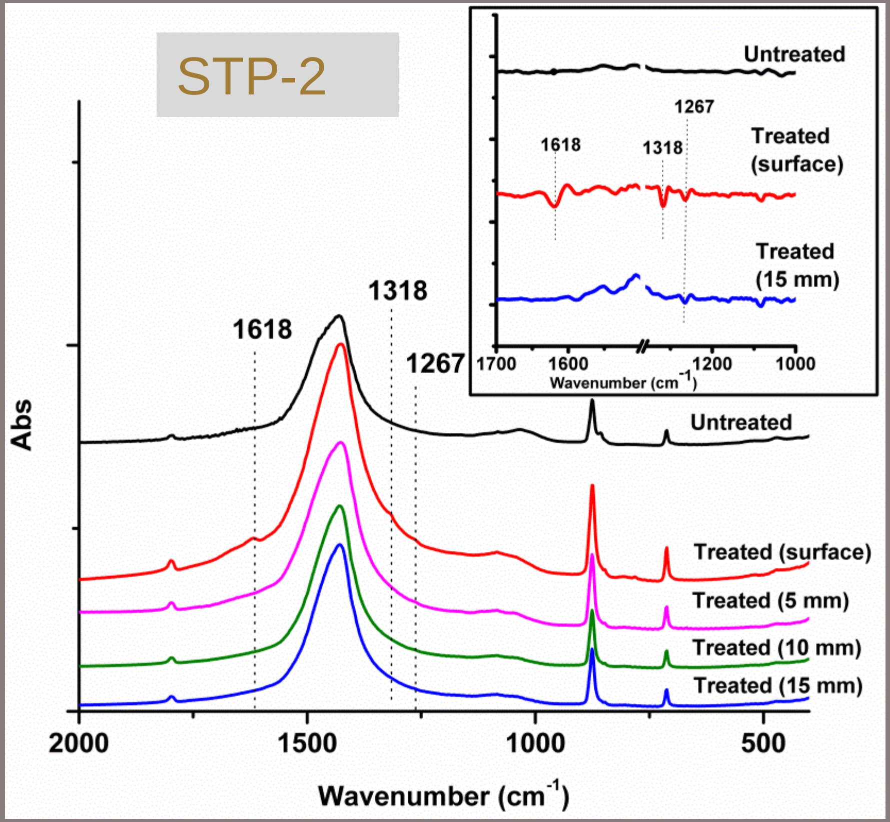
➢Mechanical properties and penetration depth



1. Increase of the mechanical resistance
2. A penetration depth of approximately 15 mm

Effectiveness of the nanocomposites as consolidant on limestone

➤Mechanical properties and penetration depth



Chemical compatibility

1. <u>1267 cm^{-1}</u>

$-CH_3$ groups of $Si-(CH_3)$ of PDMS

Exists in the spectra of 15 mm (2^{nd} derivative)

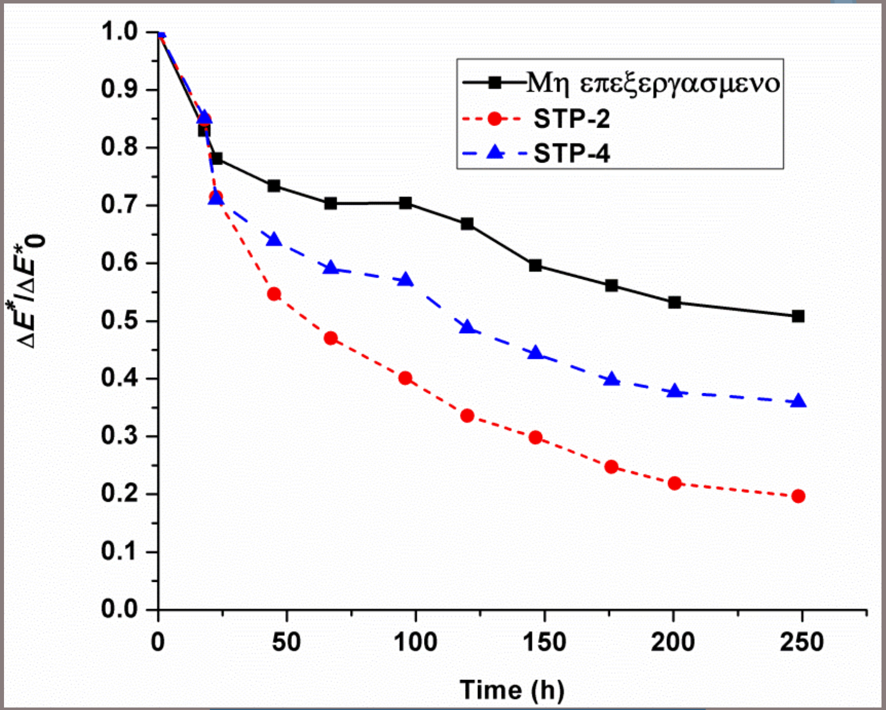
2. <u>1618 and 1318 cm^{-1}</u>

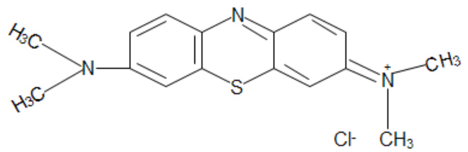
Calcium Oxalate (on the surfaces)

1. is more stable than $CaCO_3$
2. can act protectively against the weathering deterioration

Effectiveness of the nanocomposites as consolidant on limestone

Self-cleaning limestone





Μπλε του μεθυλενίου
(*Methylene Blue , MB*)

➢The results match perfectly with those obtained from the photocatalytic tests of the nanocomposites

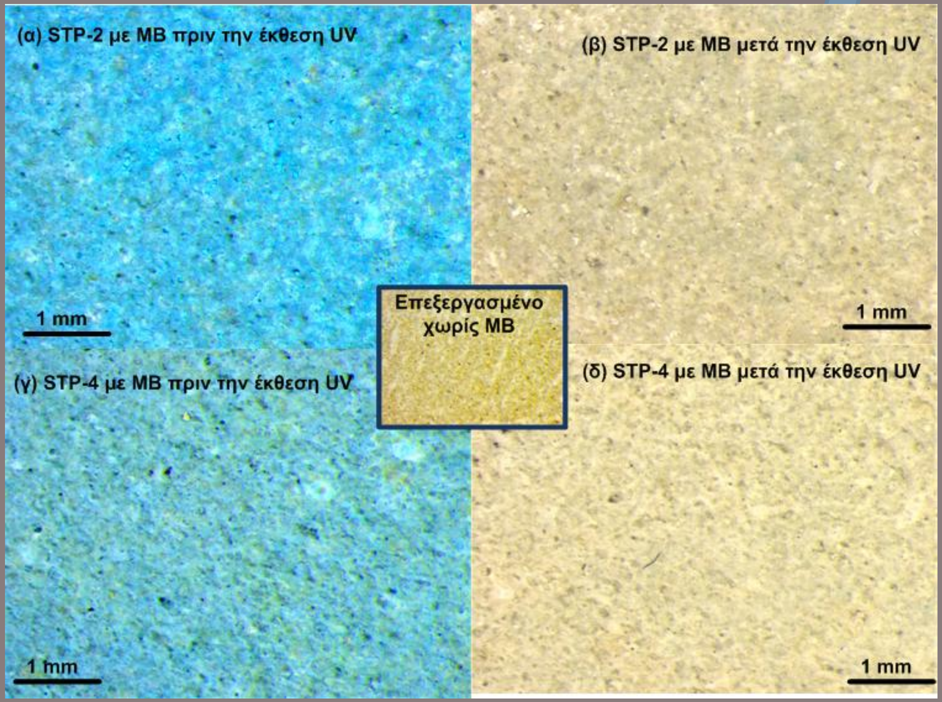
STP-2>STP-4

STP-2 higher than STP-4 activity due to the presence of greater amount of crystals, as observed by TEM

Effectiveness of the nanocomposites as consolidant on limestone

Self-cleaning limestone

Optical Microscopy
Before and after 250 h UV irradiation



➢ These results confirm that STP-2 presents the better photocatalytic behavior.
The most effective color removal has been observed on the marble treated with STP-2

Conclusions

- Three **homogeneous**, **highly transparent** and **hydrophobic** nanocomposites were synthesized (STP-1, STP-2, STP-4)
- Synthesis of photocatalytically active **anatase TiO_2** in **room temperature in the presence of Oxalic acid**
- Successful **incorporation of** TiO_2 nanoparticles (with size 5 to 10 nm) into the **silica matrix** through the mixing of both of Si and Ti alkoxides
- **Effective control** of TTIP hydrolysis through the **chemical modification** with the **Oxalic acid**
- **The nanocomposites present a cohesive structure without the presence of crackings**

Conclusions

- ✓ The presence of PDMS reverses the hydrophilic character of the SiO_2-TiO_2 system to **hydrophobic**
- ✓ The **photocatalytic activity** of the nanocomposites was confirmed through the decomposition of Methyl Orange and Methylene Blue (STP-2>STP-4>STP-1)
- ✓ Confirmation of the multiple role of the Oxalic acid:
  - **catalyst**
  - **low values pH (removal from the IEP)**
  - **chelating nucleophilic reagent**
  - **facilitation of anatase TiO_2**
  - **DCCA**
  - **calcium oxalate**
  - **hole-scavenger during the photocatalytic process**

Conclusions

- ✓ Chemical compatibility nanocomposites and stones:
  1. **absence of undesirable byproducts** and
  2. formation of **Calcium Oxalate** on stone surfaces can further **protect the substrates**
- ✓ The novel nanomaterials induce **hydrophobic properties** to the stone substrate **without altering the color** of the substrate and allowing **the water vapor permeability**
- ✓ The nanomaterials, STP-2 and STP-4, can effectively function as **consolidant agents**
- ✓ Also, the **photocatalytically** active nanocomposites preserve the stone's surfaces from the dirt accumulation
- ✓ These developed novel nanotechnology materials can be further produced on an **industrial scale** (Eco-friendly, Friendly and convenient for the users, Low cost materials)

Recommendations for further work

- ✓ Application and estimation of the effectiveness of the nanocomposites to more substrates, such as lime and cement mortars
- ✓ Salt ageing of treated marbles, limestones and mortars
- ✓ *In situ* evaluation of self-cleaning properties
- ✓ Antibacterial studies of the synthesized nanocomposites
- ✓ Characterization of the nanocomposites through X-Ray Absorption Near Edge Structure, XANES

Publications

International Scientific Journals

1. «Producing photoactive, transparent and hydrophobic SiO_2-crystalline TiO_2 nanocomposites at ambient conditions with application as self-cleaning coatings», Chrysi Kapridaki, Luís Pinho, Maria J. Mosquera, Pagona Maravelaki-Kalaitzaki, Applied Catalysis B: Environmental 156–157 (2014) 416–427. (cited by 1)
2. «TiO_2–SiO_2–PDMS nano-composite hydrophobic coating with self-cleaning properties for marble protection», C. Kapridaki and N. Maravelaki-Kalaitzaki, Progress in Organic Coatings, 76, 2013, pp. 400-410. (cited by 19, Most download 14th January 2015)

International Scientific Books (Peer-reviewed)

3. «TiO_2–SiO_2–PDMS nanocomposites with self-cleaning properties for stone protection and consolidation» Chrysi Kapridaki & Noni-Pagona Maravelaki [year]. In: Přikryl, R., Török, Á, Gómez-Heras, M., Miskovsky, K. & Theodoridou, M. (eds) Sustainable Use of Traditional Geomaterials in Construction Practice. Geological Society, London, Special Publications, 416. First published online [month] [date], [year], http://dx.doi.org/10.1144/SP416.6
4. «Improvement of properties of hydraulic mortars with addition of nano-titania», N. Maravelaki, C. Kapridaki, E. Lionakis, A. Verganelaki. In D. Croccolo (eds) Adhesives, Mechanical Properties Technologies and Economic Importance, Nova Science Publishers, Inc, 2014, p.79-92.

Publications

International Scientific Conferences (Review in full text)

5. «SiO_2-crystalline TiO_2 Photoactive and Hydrophobic Nanocomposites with Application as Self-cleaning Coatings on Buildings», Luís Pinho, Chrysi Kapridaki, Maria J. Mosquera, Pagona Maravelaki-Kalaitzaki, 8th European Meeting on Solar chemistry and photocatalysis: Environmental Applications, 25-28 June, 2014, Thessaloniki, Greece
6. «Improvement of properties of hydraulic mortars with addition of nano-titania», N. Maravelaki, C. Kapridaki, E. Lionakis, A. Verganelaki, 3rd Historic Mortars Conference,11-14 September 2013, Glasgow, Scotland.
7. «TiO_2-SiO_2-PDMS nano-composite hydrophobic coating with self-cleaning properties for marble protection», C. Kapridaki and N. Maravelaki-Kalaitzaki, 12th International Congress on the Deterioration and Conservation of Stone, 22-26 October, New York.
8. «Characterization of hydraulic mortars containing nano-titania for restoration applications», N. Maravelaki, E. Lionakis, C. Kapridaki, Z. Agioutantis, A. Verganelaki, E. Aggelakopoulou and V. Perdikatsis, 12th International Congress on the Deterioration and Conservation of Stone, 22-26 October, New York .
9. «Physico-chemical and mechanical characterization of hydraulic mortars containing nano-titania for restoration applications», P. Maravelaki-Kalaitzaki, E. Lionakis, Z. Agioutantis, C. Kapridaki, A. Verganelaki, S. Mayrigianakis, M. Stavroulaki, V. Perdikatsis, N. Kallithrakas-Kontos, 4th International Symposium on Nanotechnology in Construction- NICOM 4, May 20-22, 2012, Agios Nicolaos, Crete, Greece

Awards

1. Το Πρόγραμμα της Μονάδας Καινοτομίας και Επιχειρηματικότητας του Πολυτεχνείου Κρήτης επέλεξε και χρηματοδότησε μερικώς την έρευνα με τίτλο: «**Νάνο-σύνθετα αυτοκαθαριζόμενα-προστατευτικά υμένια δομικών υλικών**» στα πλαίσια του προγράμματος, **Φυτώριο Ιδεών Ι, 2011-2012**, που αφορούσε καινοτόμες Ιδέες φοιτητών.
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   (**1st award: «Ecological nanomateriasl for the protection against the decay of modern and traditional buildings»**, 2nd Competition for Applied Research and Innovation, MAICh-R&D INDUSTRY (2013)

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Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

Ευχαριστώ για την προσοχή σας

Thank you for your attention

First