Research and applications of nanomaterials in Cultural Heritage

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UNIVERSITÀ DELLA CALABRIA

University of Calabria Campus

- 14 Departments
- 34500 Students
- 836 Professors & Researchers
- 200 hectares of surface
- 3000 sleeping accommodations
- Canteens: 3500 meals each day
- 2 theatres

University of Calabria Campus


Research group on Science applied to Cultural Heritage
Gino M. Crisci (Full professor)
Donatella Barca (Associate professor)
Mauro F. La Russa (Researcher)
Domenico Miriello (Researcher)
Silvestro A. Ruffolo (Research fellow)
Michela Ricca (Research fellow)
Natalia Rovella (Contractor)
Raffaella De Luca (Contractor)
Valeria Comite (Contractor)


Topics of our research (stone materials)
Archeometric Analysis
Knowledge of materials
Provenance analysis
Scientific Support to Restoration and Conservation
Degradation
Conservation strategies

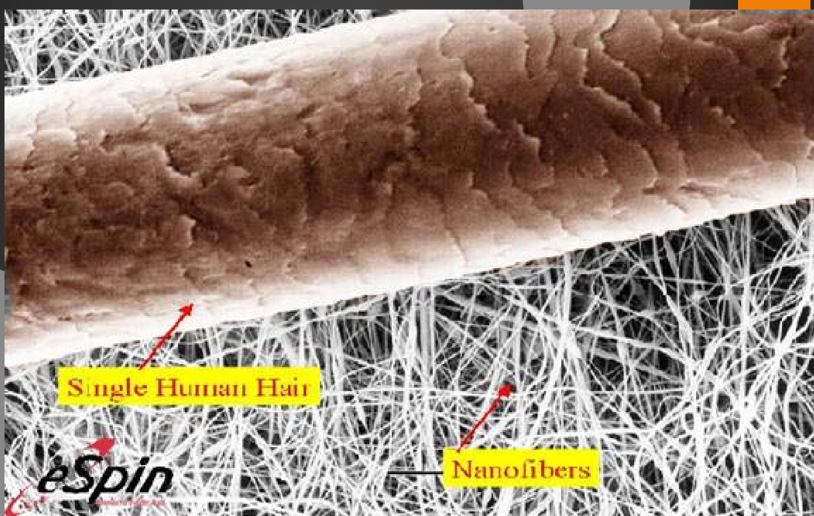
Overview of the lecture

- What is nanotechnology
- Why we should apply nanotechnology to restoration of Cultural Heritage
- State of art of research
- Consolidation with nanoparticles
- Protection with nanoparticles

https://kahoot.it

What is Nanotechnology

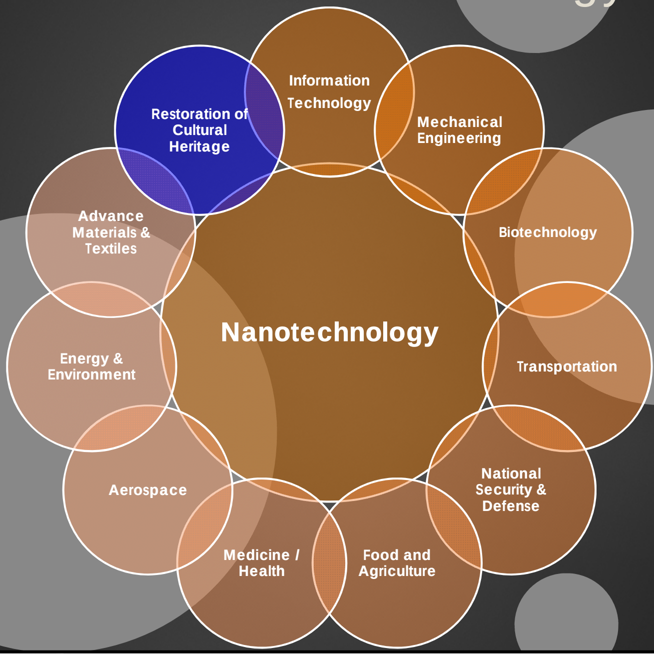
The study of the controlling of matter on an atomic and molecular scale. Generally nanotechnology deals with structures sized between 1 to 100 nanometres in at least one dimension, and involves developing or modifying materials or devices within that size.



A Human Hair is about 100 µm wide

Source: http://sintefi.blogspot.it/2013/05/nanofibra.html

Applications of nanotechnology



Applications of nanotechnology in Cultural Heritage

Why we should use nanoparticles in restoration?

Example: for consolidation of stone materials, there is the need of small particles in order to achieve a deeper penetration

Limewater and milk of lime

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

Solubility of $Ca(OH)_2$ = 1.7 g/l (0.17%)

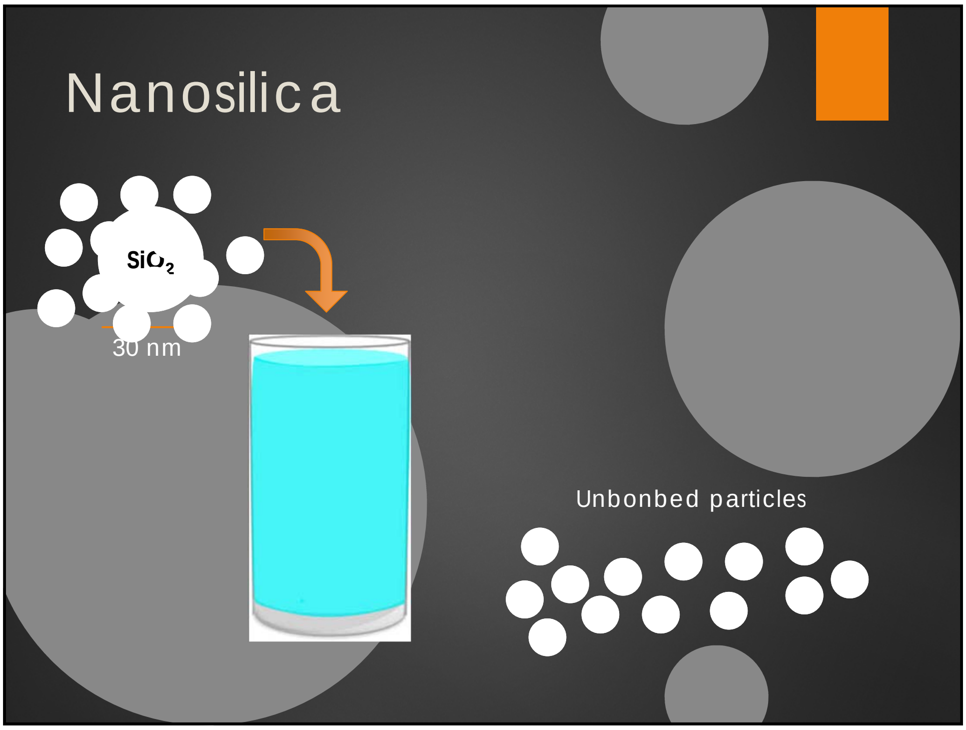
A satured solution of $Ca(OH)_2$ is called limewater

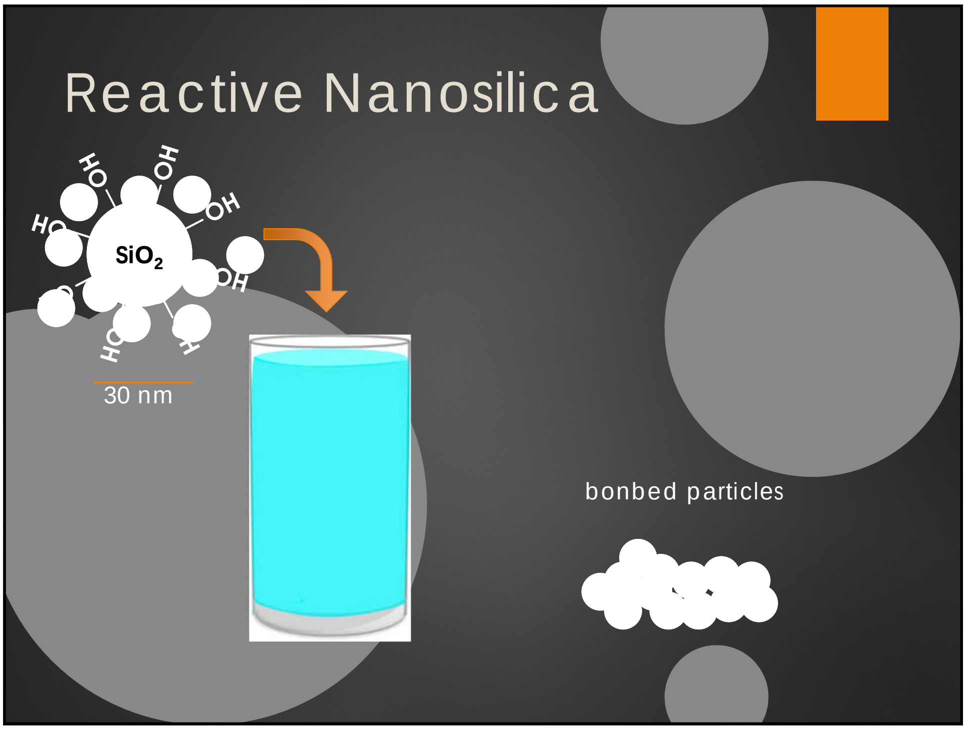
Limewater and milk of lime

If I add more lime I will obtain a milky suspension called milk of lime

The main problem is related the dimension of the particles (scarce penetration)

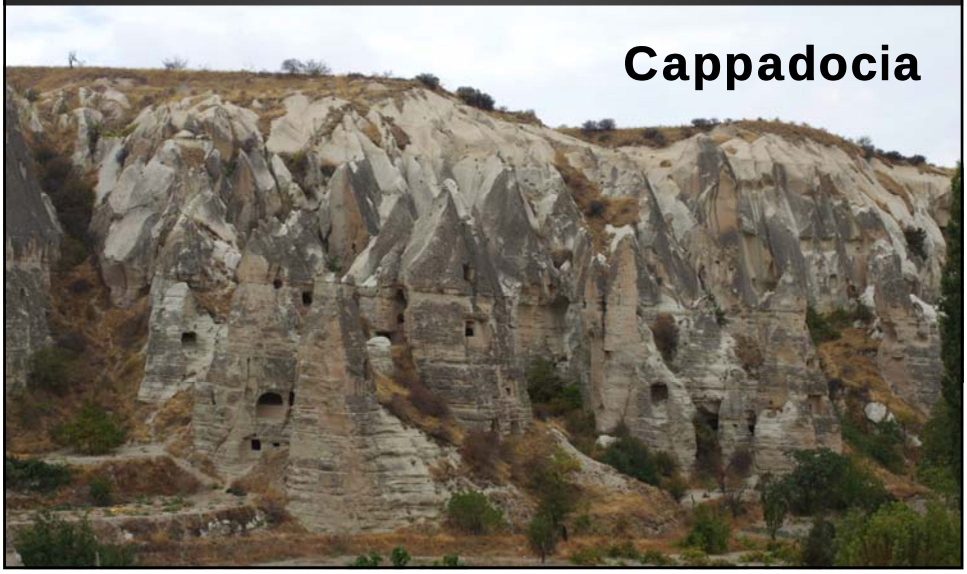

nanolime
200 nm
Baglioni & Giorgi 2006


Nanosilica
SiO_2
30 nm
Unbonbed particles


Reactive Nanosilica
SiO_2
OH
30 nm
bonbed particles

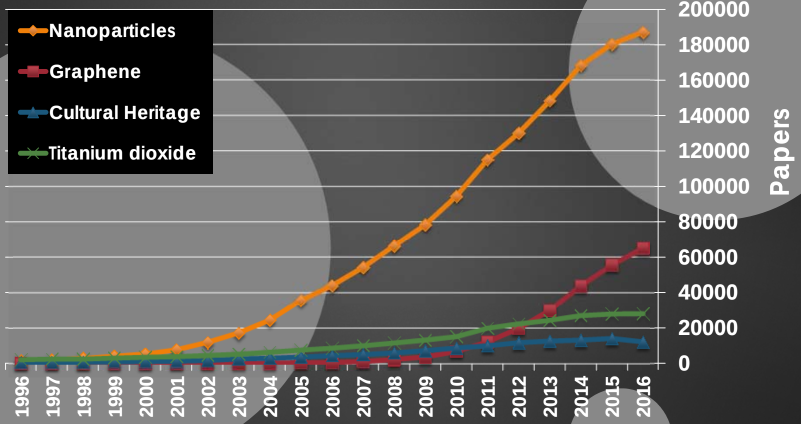

Nanosilica as consolidant for stone
Strenghts
- Water based
- Less sensitive to microclimatic conditions
- Quick curing
Weaknesses
- Penetration depht
SWOT
Opportunities
- Use as binder for mortars
Threats
- Flocculation with salts
- Best practice issues

Testing nanosilica

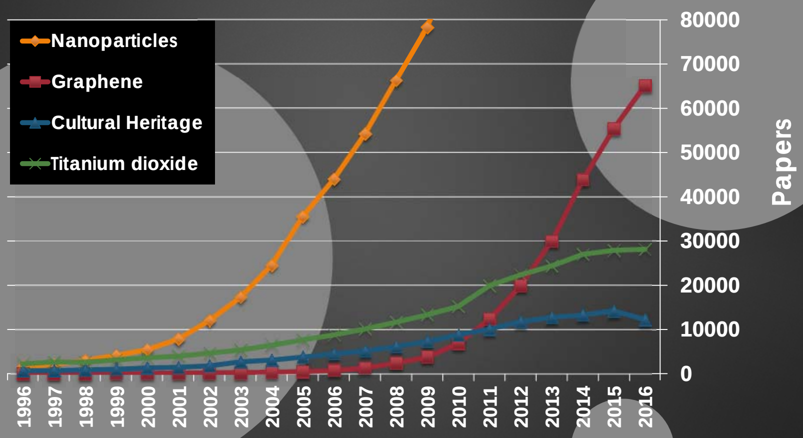


Testing nanosilica

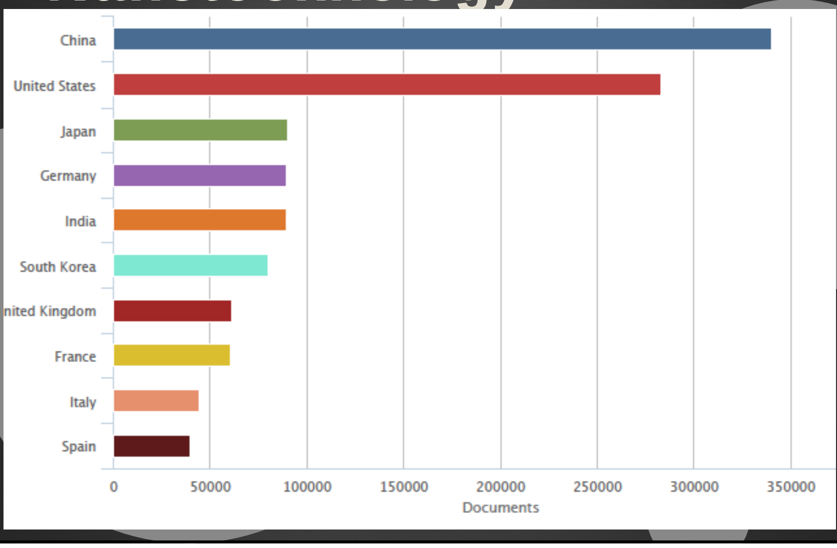
Nanotechnology and Cultural Heritage
A survey in SCOPUS database

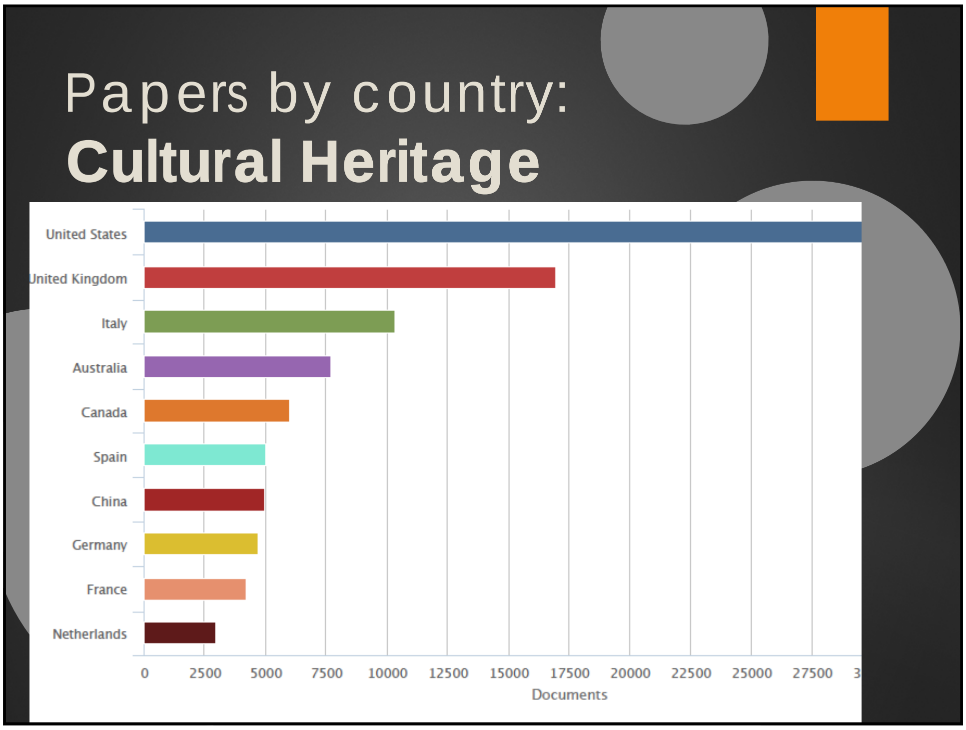


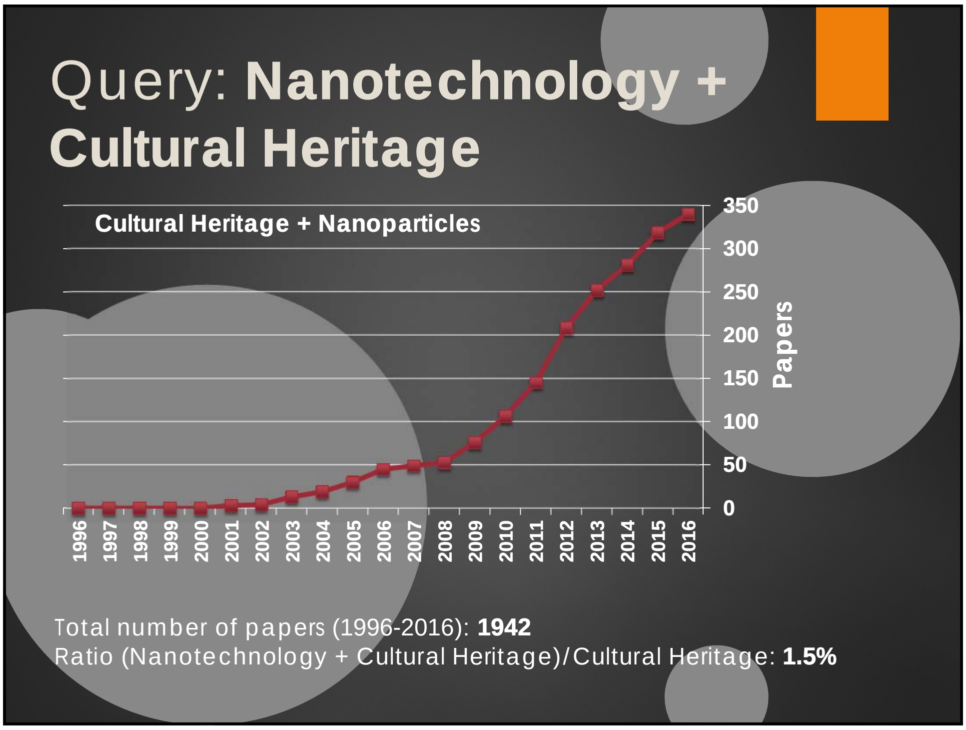
Nanotechnology and Cultural Heritage
A survey in SCOPUS database



Papers by country: **Nanotechnology**

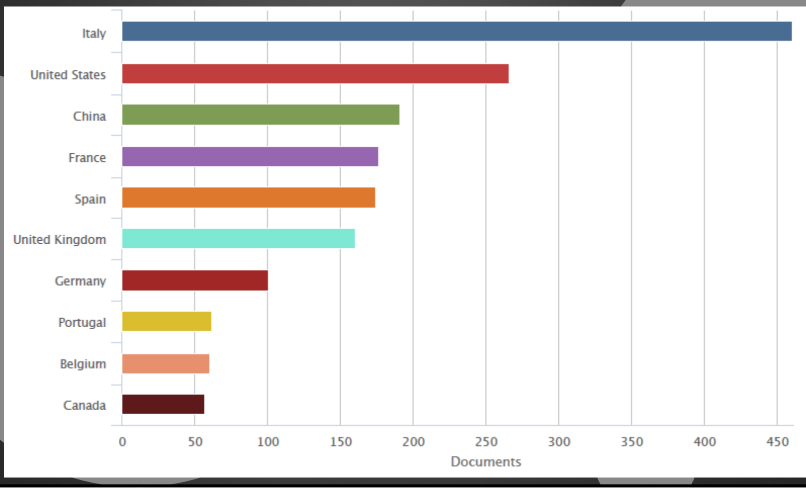



Papers by country:
Cultural Heritage
United States
United Kingdom
Italy
Australia
Canada
Spain
China
Germany
France
Netherlands
0
2500
5000
7500
10000
12500
15000
17500
20000
22500
25000
27500
Documents

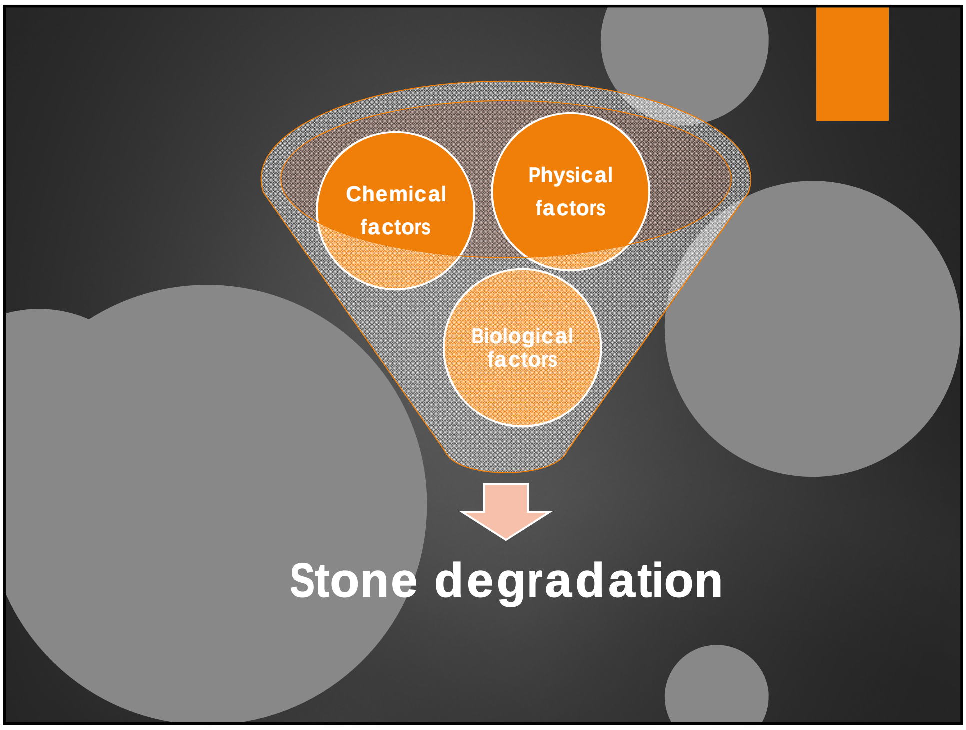

Query: Nanotechnology +
Cultural Heritage
Cultural Heritage + Nanoparticles
350
300
250
200
150
100
50
0
Papers
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
Total number of papers (1996-2016): 1942
Ratio (Nanotechnology + Cultural Heritage)/Cultural Heritage: 1.5%

Query: **Nanotechnology + Cultural Heritage**

Papers by country

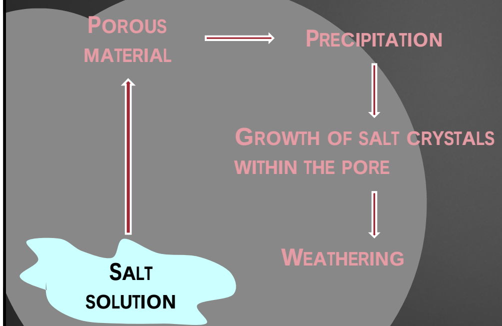


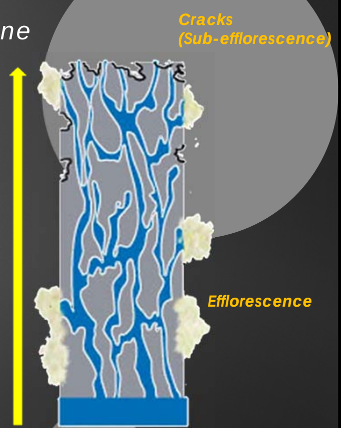
Some examples

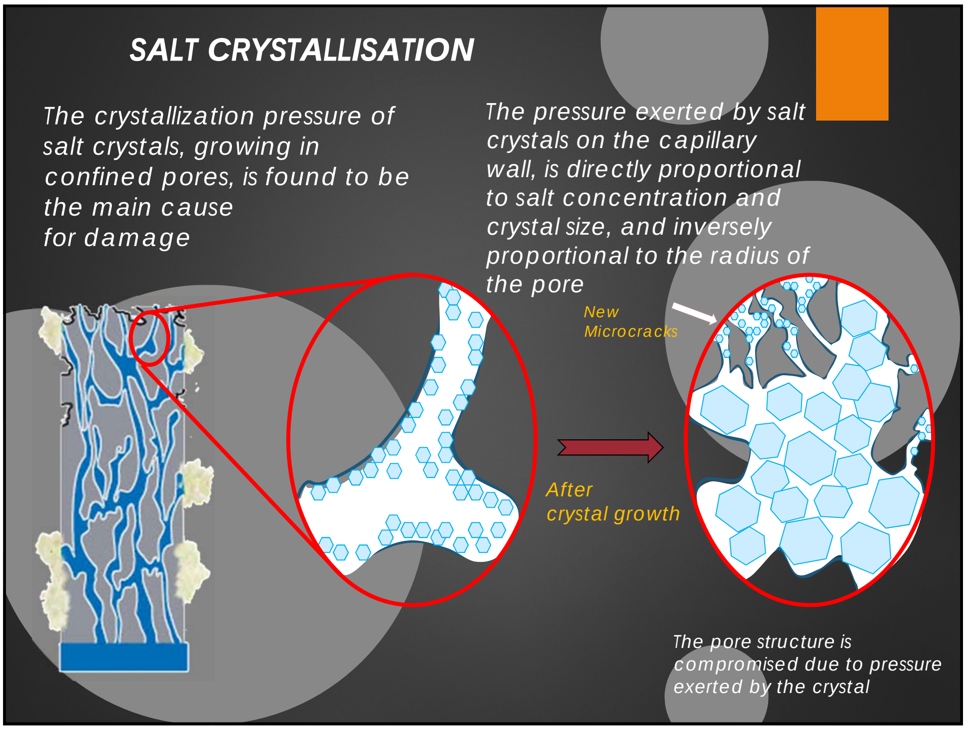


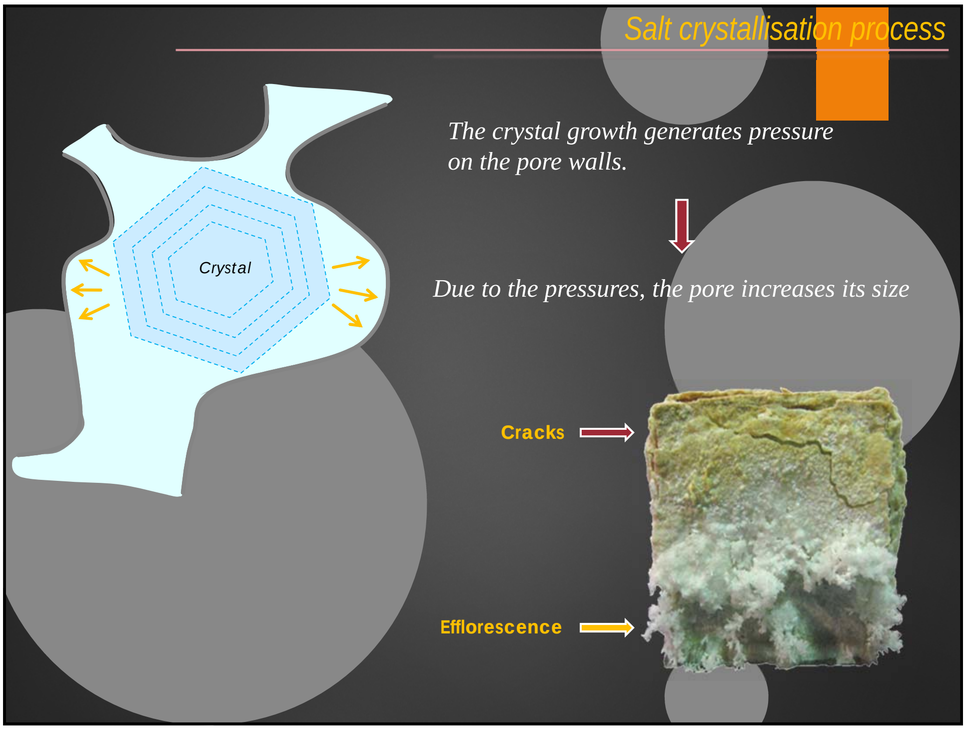
SALT CRYSTALLISATION

When a salt-rich solution penetrates into the pore structure, in specific supersaturating and thermodynamic conditions, the salt crystallization takes place and nucleation and growth of salt crystals within the pore spaces can induce alteration and degradation of the stone






SALT CRYSTALLISATION
The crystallization pressure of salt crystals, growing in confined pores, is found to be the main cause for damage
The pressure exerted by salt crystals on the capillary wall, is directly proportional to salt concentration and crystal size, and inversely proportional to the radius of the pore
New Microcracks
After crystal growth
The pore structure is compromised due to pressure exerted by the crystal


Salt crystallisation process
The crystal growth generates pressure on the pore walls.
Due to the pressures, the pore increases its size
Crystal
Cracks
Efflorescence


Salt crystallization + wind = Alveolization

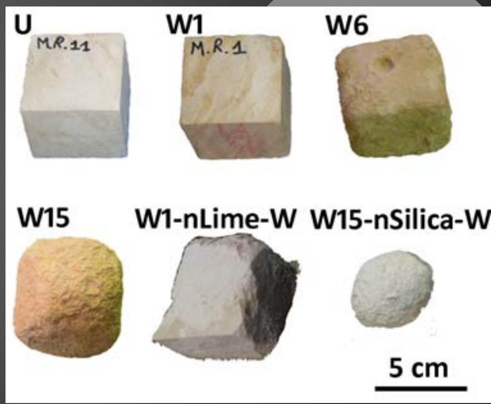

Alveolization?

New insights on the *CONSOLIDATION* of salt weathered limestone: the case study of Modica Stone

Nanosilica

Nanolime

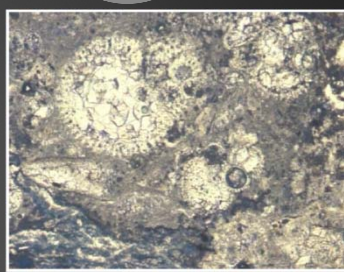
TEOS - Ethyl Silicate



Ruffolo et al 2015, Bulletin of Engineering Geology and the Environment

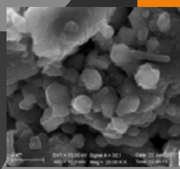
Modica stone

- Petrographic observations (Belfiore et al. 2010) revealed a grain-supported texture with about 30% of micritic matrix. Allochemical components, with percentages between 40 and 45%, consist of several bioclasts.

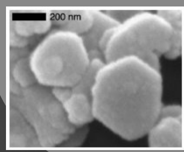


The porosity (about 27%) is mainly intergranular. According to Dunham (1962), the Modica stone can be classified as a packstone, according Folk (1962) as a biomicrite.

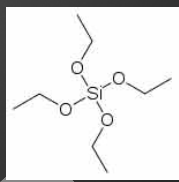
- Nanosilica is a water suspension of reactive silica nanoparticles having size 50-100 nm

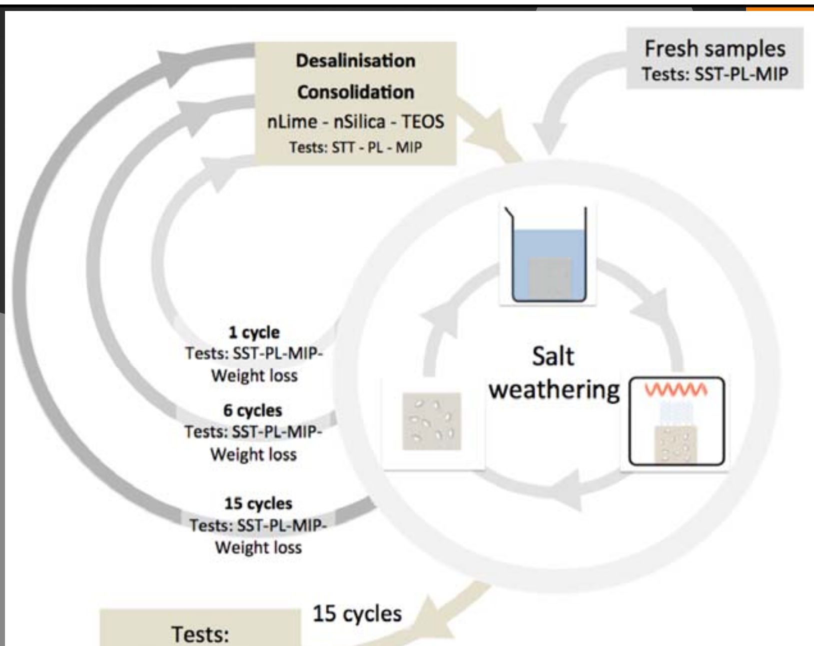


- Nanolime is a suspension of Calcium Hydroxide nanoparticles in alcohol having size 100-200 nm



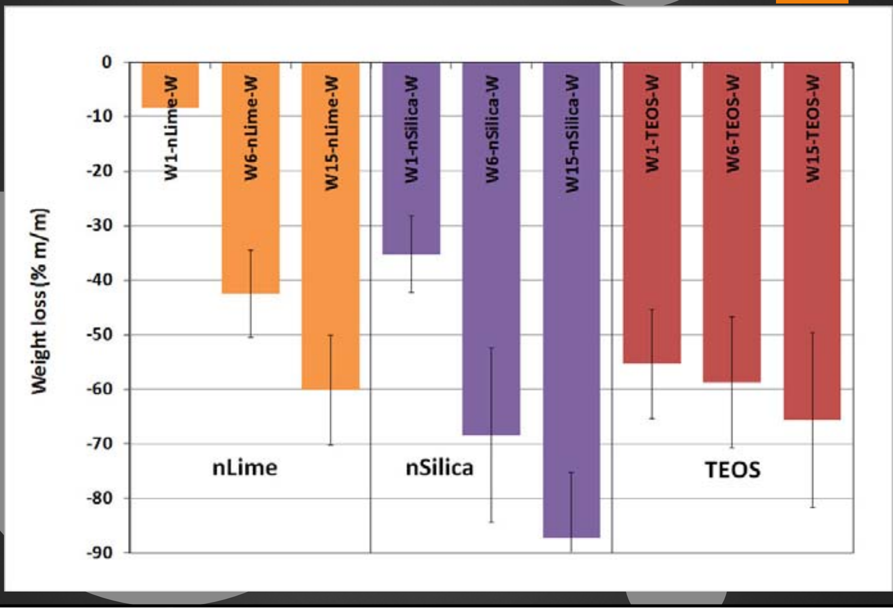
- TEOS – Ethyl Silicate 30% w/w diluted in white spirit



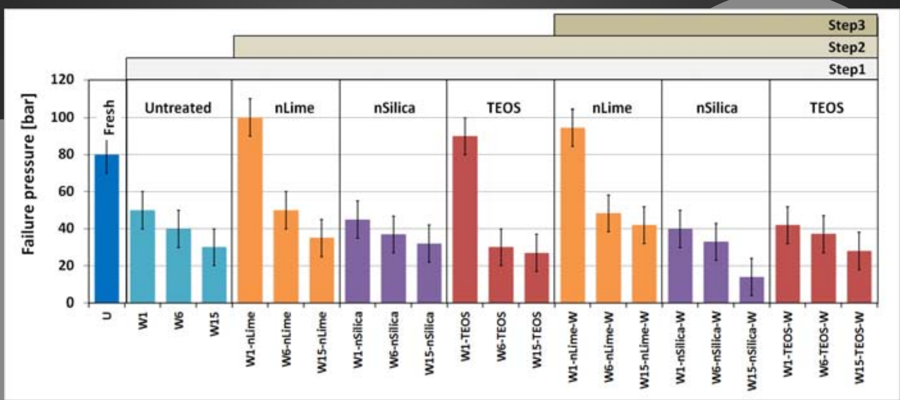


Ruffolo et al 2015, Bulletin of Engineering Geology and the Environment

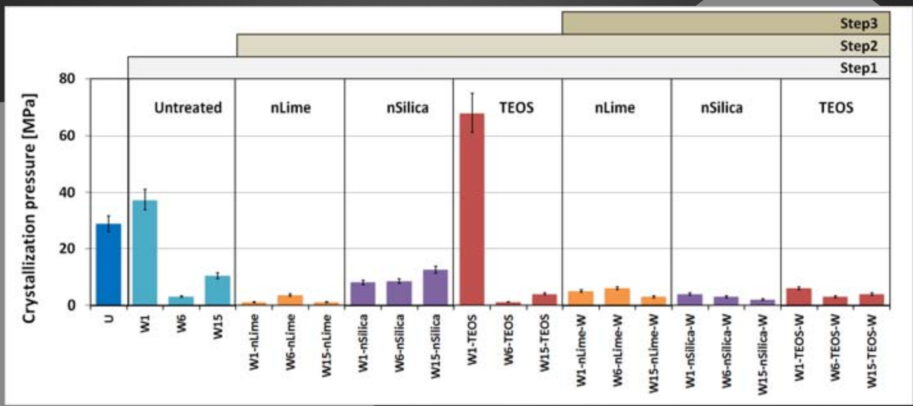
Weight loss



Point load test



Crystallization pressure



PHOTOCATALYTIC TITANIUM DIOXIDE FOR THE MITIGATION OF BIOCOLONIZATION ON STONE MATERIAL

Ruffolo et al.

Submitted to International Biodeterioration & Biodegradation

Biological degradation of stone surfaces

Use of biocides in restoration of stone surfaces

- In the early stages of cleaning of an area affected by biological degradation, a fundamental operation is represented by the removal of biological patinas
- The removal of biological patinas requires the use of biocides (organic compounds in aqueous or organic solvent)
- The removal of biological patinas does not ensure an inhibiting effect over time

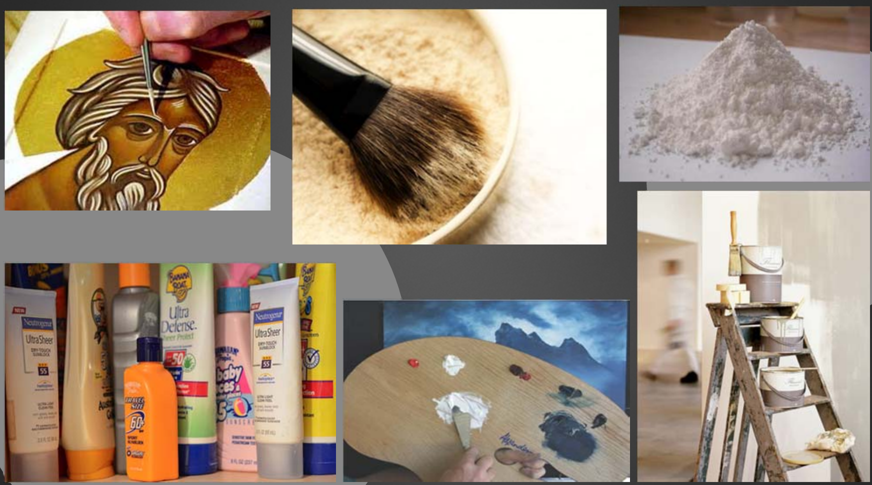
Removal of biological patinas

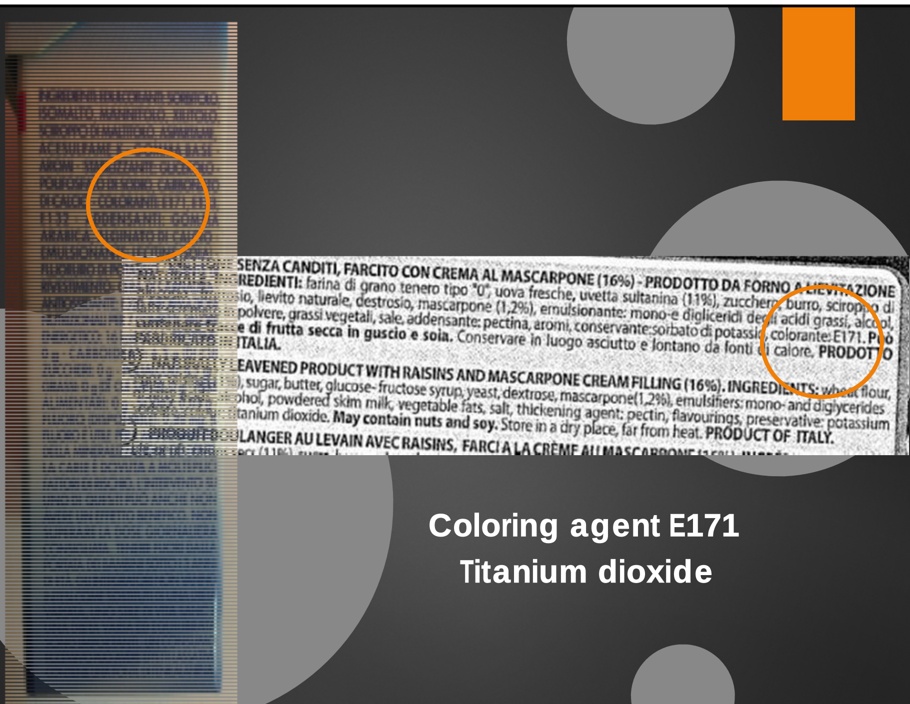
Conservation “philosophy”

A product that can assure an inhibition effect can produce benefits:

- Economic: less cleaning interventions over time for the removal of biological patina
- Environmental: linked to reduced use of biocides and solvents

Titanium dioxide





Coloring agent E171
Titanium dioxide

Crystalline phases of TiO_2

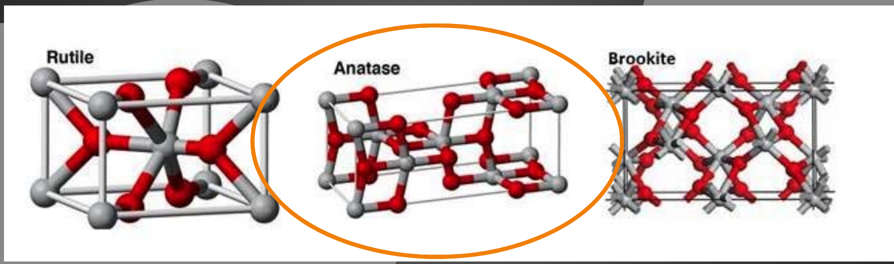
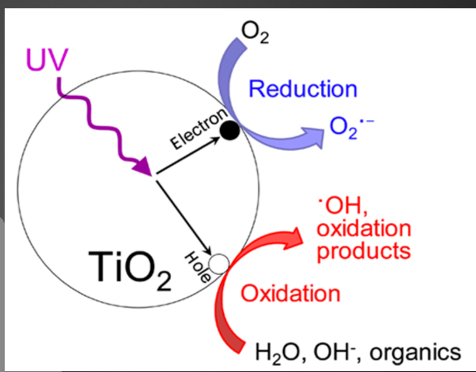
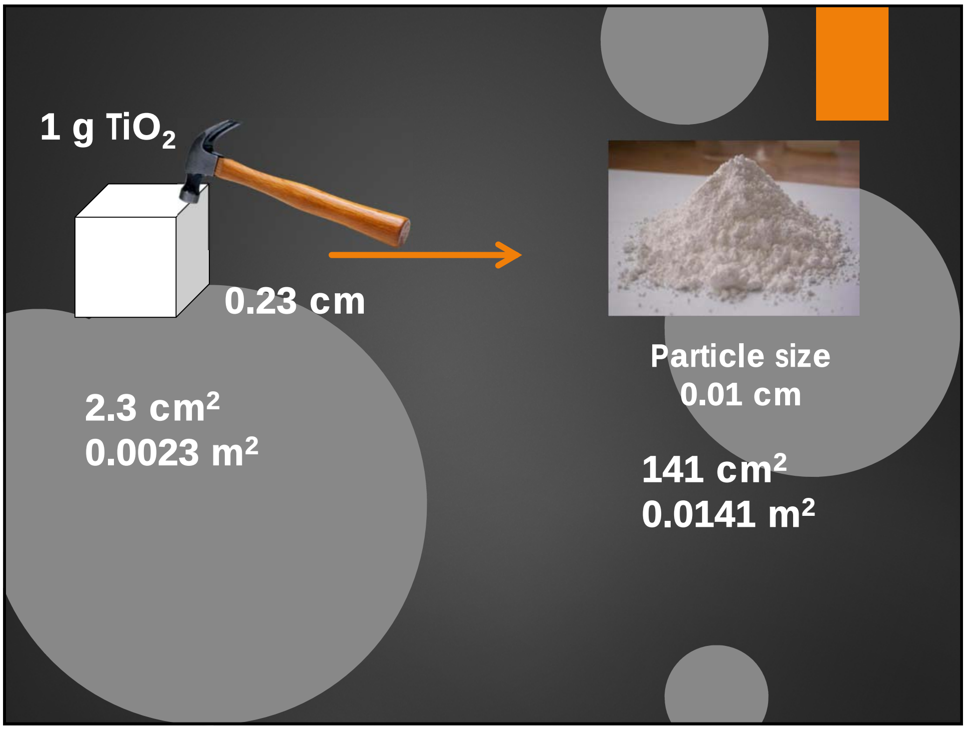


Photo-catalytic effect

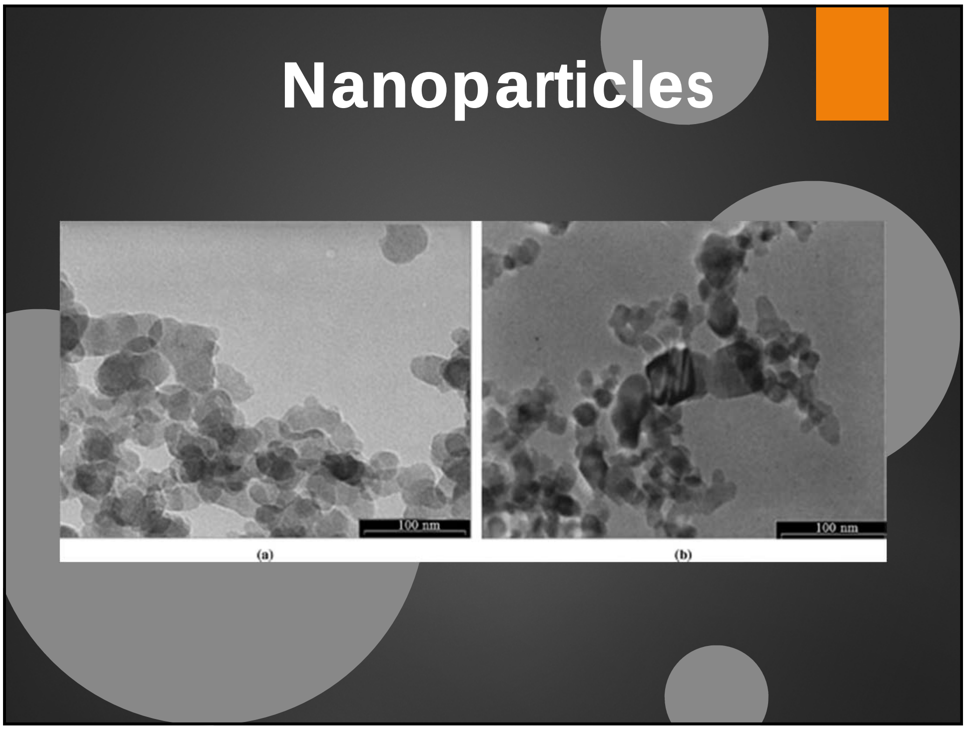
UV light
< 390 nm



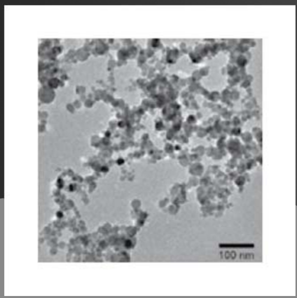
Self cleaning effect and biocidal effect occurs on titania surface



1 g TiO_2
0.23 cm
2.3 cm²
0.0023 m²
Particle size
0.01 cm
141 cm²
0.0141 m²



Nanoparticles
100 nm
100 nm
(a)
(b)



1g TiO_2
Particle size 25 nm:

300 m^2

40 g TiO_2
12000 m^2

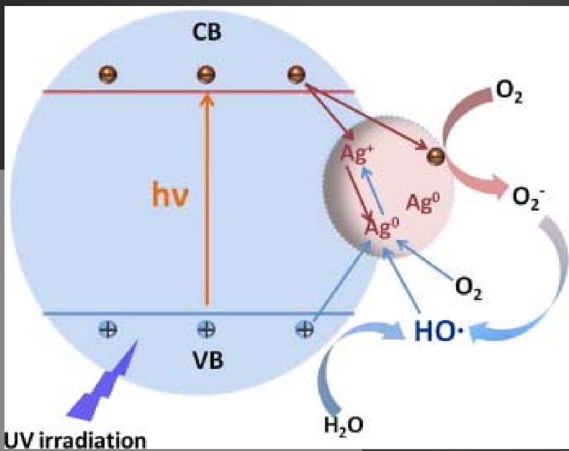
M-Doped TiO_2

By doping the TiO_2 it is possible to enhance the efficiency → In literature many doping metals have been used for this purpose

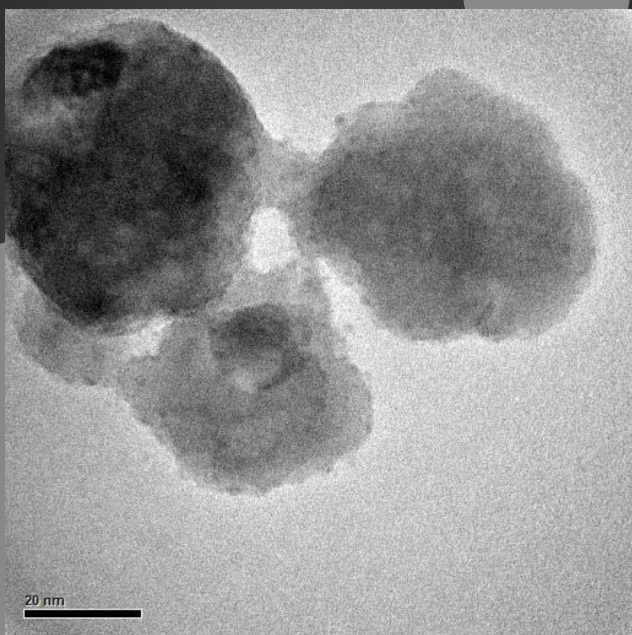
Kind of dopant	Doped element	Preparation method	Potential application
Metal dopants	Ag	Silver nitrate was mixed with reduction agent (sodium citrate tribasic dihydrate) and the reaction temperature was raised to 80°C with continuous stirring. Then TIP and HNO_3 were added and the reaction was maintained at 50°C for 24 h. The prepared sol was dried at 105°C for 24 h and calcined at 300°C.	Degradation of nitrophenol in aqueous phase
	Fe	The reactive magnetron sputtering method: 99.99% titanium target and 99.9% iron pieces were placed in the reaction chamber and mixture of argon and oxygen was introduced into the chamber during discharging.	Wastewater decoloring
	V	Sol-gel method: Solution 1 (vanadyl acetylacetonate dissolved in n-butanol) was mixed with solution 2 (acetic acid in titanium butoxide) and hydrolyzed (24 h) by the water generated via the estrification of acetic and butanol. The suspension as dried at 150°C, pulverized and calcined at 400°C for 0, 5 h.	Wastewater decoloring
	Au	Titanium (IV) butoxide dissolved in absolute ethanol was added to solution containing tetrachloroauric acid ($HAuCl_4 \cdot 4H_2O$), acetic acid and ethanol. The resulting suspension was aged (2 days), dried under vacuum, grinding and calcinated at 650°C.	Wastewater decoloring
	Pt	Photoreduction process: TiO_2 was suspended in a mixture of hexachloroplatinic acid in methanol. The suspension was irradiated with a 125 W mercury lamp (60 min.). Pt-TiO_2 was separated by filtration, washed with distilled water and dried at 100°C for 24 h.	Wastewater decoloring

Zaleska, 2008

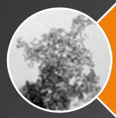
Ag-Doped TiO_2



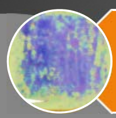
- Ag-doped titania enhances the photocatalitic effect
- Free silver can act itself as antimicrobics
- The colour become darker



Experimental



Synthesis and physical/chemical characterization of TiO_2, and doped TiO_2



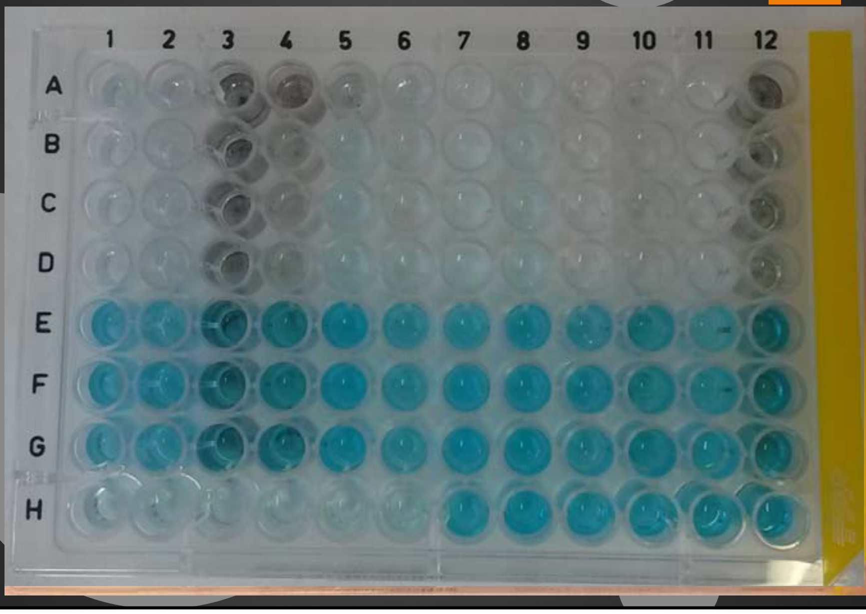
Efficiency assessment
In vitro biological experimentation
Methylene Blue degradation

Choice of the most suitable binder

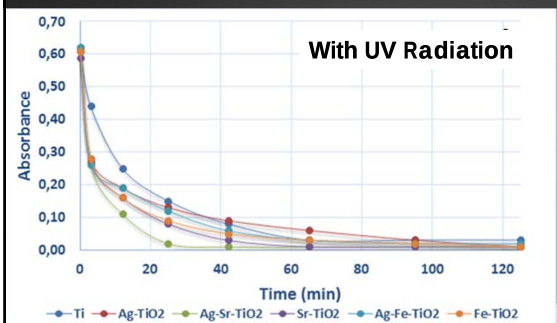
In Situ application

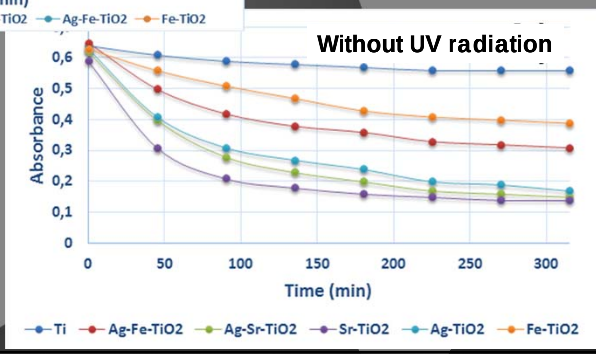
ID	material	Precursor	Acid (1 ml)	Total volume (ml)	Reaction rate
1	TiO_2	TBT	HCl 0,01M	25	Fast
2	TiO_2	TPT	HCl 0,01M	25	Fast
3	5% Ag-TiO_2	TBT	HCl 0,01M	25	Fast
4	1% Ag-TiO_2	TBT	HCl 0,01M	25	Fast
5	5% Sr-TiO_2	TBT	HCl 0,01M	25	Fast
6	1% Sr-TiO_2	TBT	HCl 0,01M	25	Fast
7	TiO_2	TPT	HCl 1M	25	Slow
8	TiO_2	TPT	HCl 1M	25	Slow
9	TiO_2	TPT	Acetic Acid 1M	25	Fast
10	TiO_2	TPT	Acetic Acid 1M	25	Fast
11	TiO_2	TPT	Acetic Acid Glacial	3	Very Slow
12	1% Ag-TiO_2	TPT	Acetic Acid Glacial	3	Very Slow

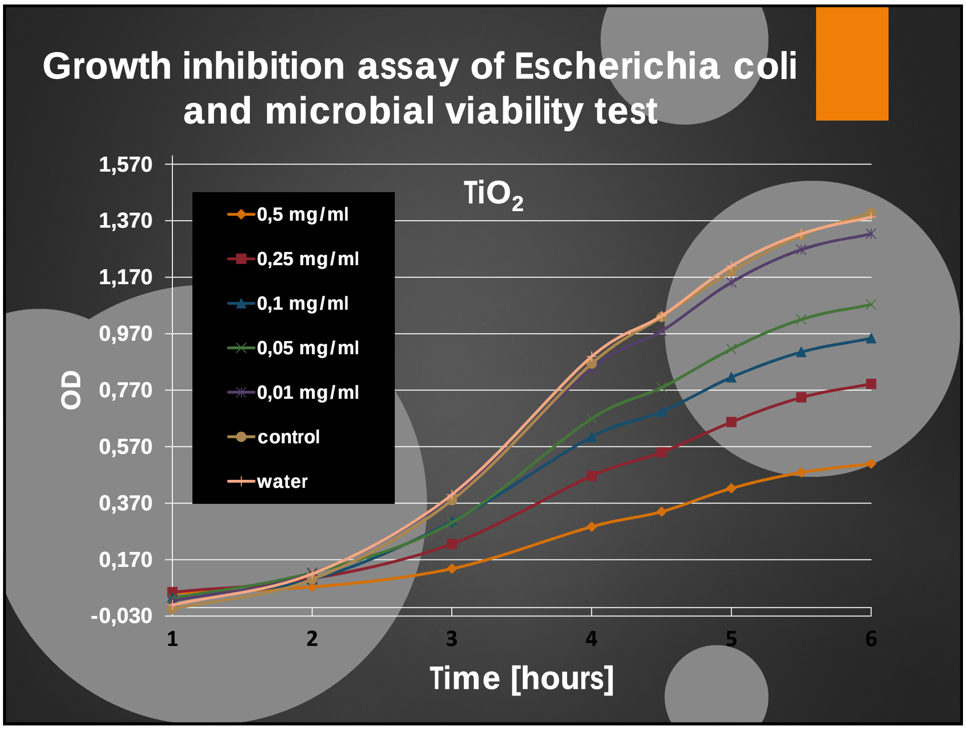
MB degradation tests

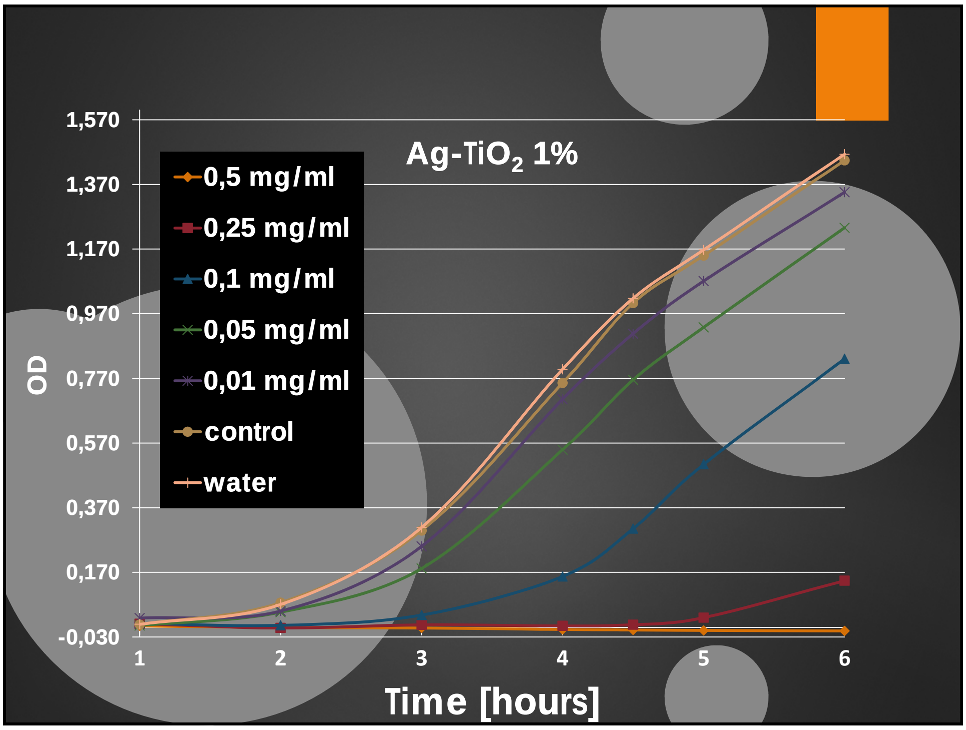


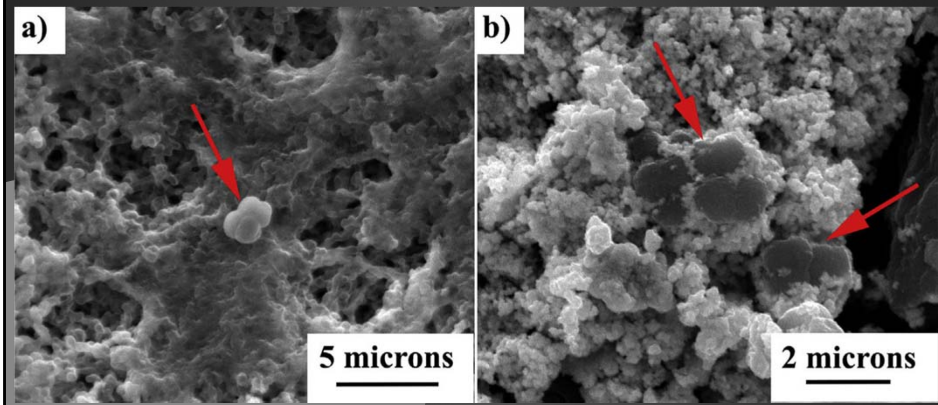
Doping effect






Growth inhibition assay of Escherichia coli and microbial viability test
TiO2
OD
1,570
1,370
1,170
0,970
0,770
0,570
0,370
0,170
-0,030
1
2
3
4
5
6
Time [hours]
0,5 mg/ml
0,25 mg/ml
0,1 mg/ml
0,05 mg/ml
0,01 mg/ml
control
water


Ag-TiO2 1%
OD
1,570
1,370
1,170
0,970
0,770
0,570
0,370
0,170
-0,030
1
2
3
4
5
6
Time [hours]
0,5 mg/ml
0,25 mg/ml
0,1 mg/ml
0,05 mg/ml
0,01 mg/ml
control
water



SEM observation of bacterial a) without contact with nanobiocides (control) and b) after 30 min of contact with AgTiO2. Bacteria result embedded into the Ag doped titania particles. Arrows indicate the bacteria

Progress in Organic Coatings 74 (2012) 186–191

Contents lists available at SciVerse ScienceDirect

Progress in Organic Coatings

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Multifunctional TiO_2 coatings for Cultural Heritage

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International Biodeterioration & Biodegradation 96 (2014) 87–96

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Testing the antibacterial activity of doped TiO_2 for preventing biodeterioration of cultural heritage building materials

CrossMark

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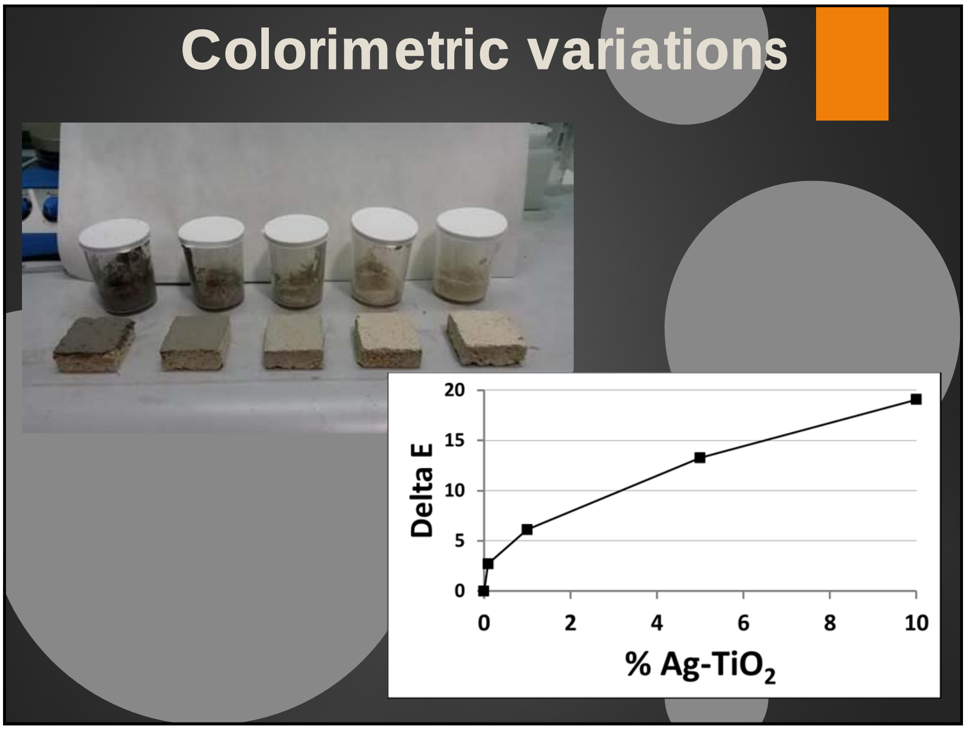
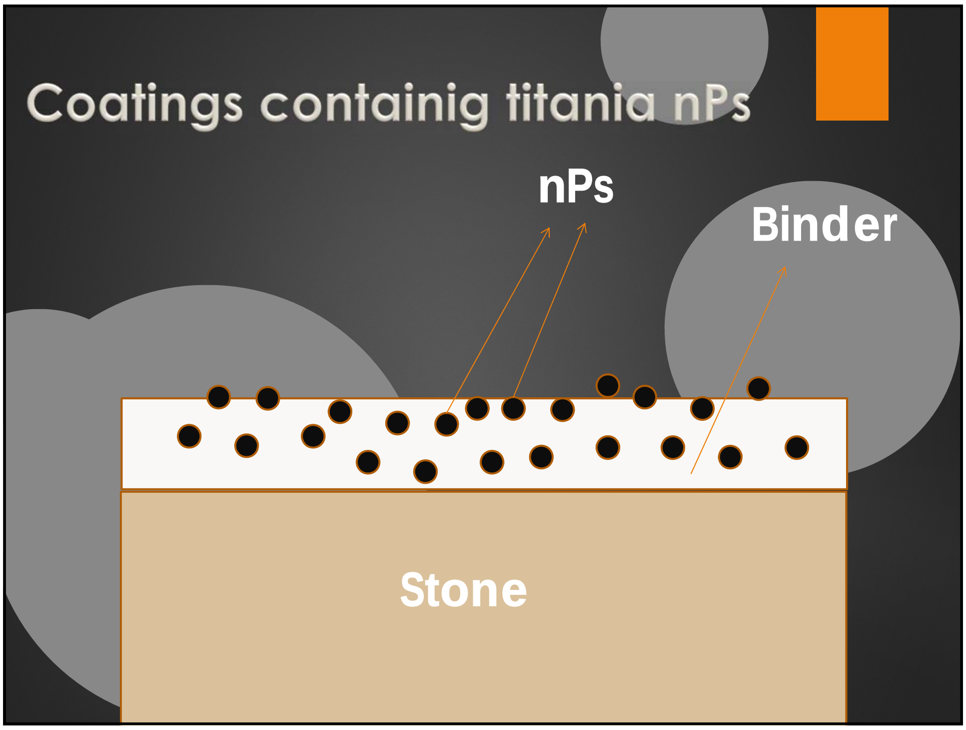
Application

Nanoparticles added to a mortar/plaster

Italian pavilion at Expo 2015 Milan


Colorimetric variations
20
15
10
5
0
Delta E
0
2
4
6
8
10
% Ag-TiO2


Coatings containig titania nPs
nPs
Binder
Stone

Choosing the binder:

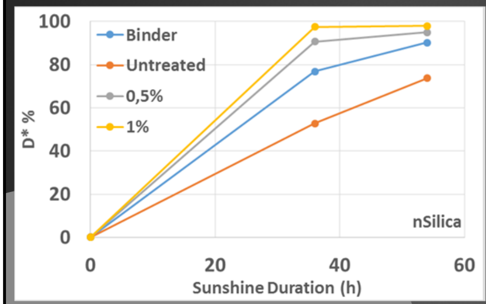
- Inorganic
- Minimal interference with the efficacy of titania

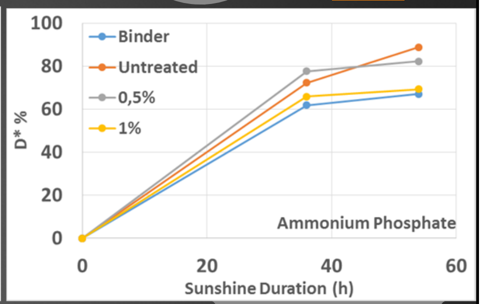
3 binders have been tested

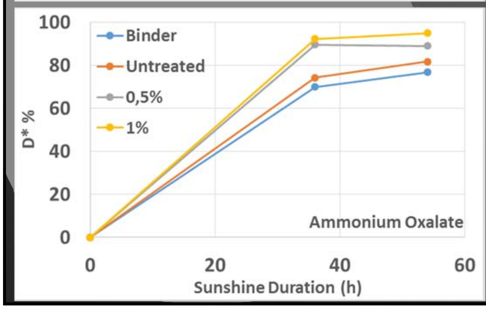
- Ammonium phosphate
- Ammonium oxalate
- NanoSilica

Blue methylene test

Blue methylene test







nanoSilica has show the best behavior, probably due to the higher pH which enhances the photocatalytic effect

In situ application

UNDERSTANDING THE BEHAVIOR OF THE COATINGS IN REAL SITUATIONS

Case studies

Choosing of the areas for experimentation

Experiment work flow

Sampling before cleaning

Samples have been taken by using a non-destructive sampling method of adhesive tape strips (Fungitape Did, Milan, Italy) as described by Urzì and De Leo, 2001)

Cleaning phase

The surfaces was first treated with a solution of Biotin R (CTS, Italy). The application has been carried out by brush. The treatment has been repeated three times (every 15 days),and then the surfaces have been rinsed with deionised water.

Experiment work flow 2

Sampling after cleaning

Samples have been collected to check the residual biocolonization

Titania treatment

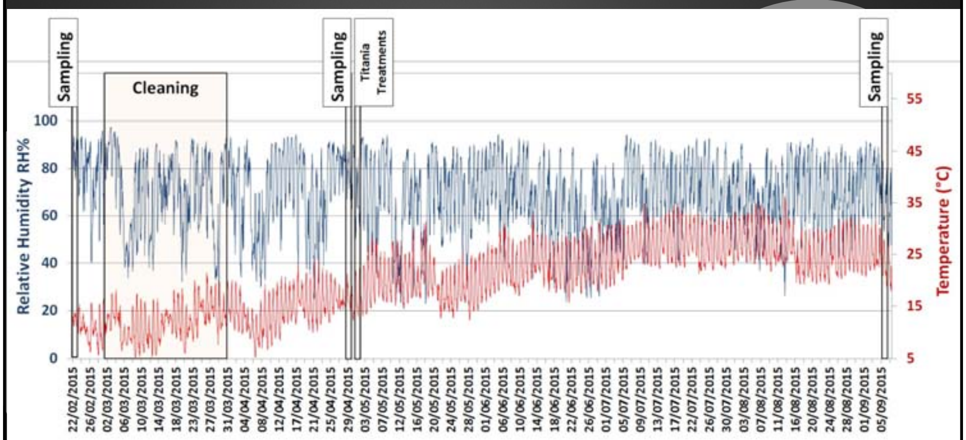
Dispersions of nanosilica and titania have been applied on stone surfaces by brush at amount of about 400 ml/m^2

Experiment work flow 3

Monitoring after TiO_2 treatment

9 samples. Check the bio inhibition feature

Experimentation timeline



Laboratory analyses

Bacterial, Fungi and Phototrophs Identification and quantification

- Microscopic observations
- SEM analysis
- Cultural analyses
- ITS-PCR for bacteria
- 16SrDNA partial sequencing for Bacteria
- DNA extraction and PCR amplification for fungi

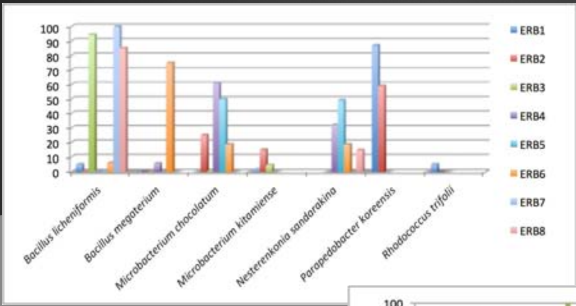
Results –before cleaning-

Table 2. Amount of chemoorganotrophic microorganisms determined as cfu/g or as different degree of abundance for phototrophic ones.

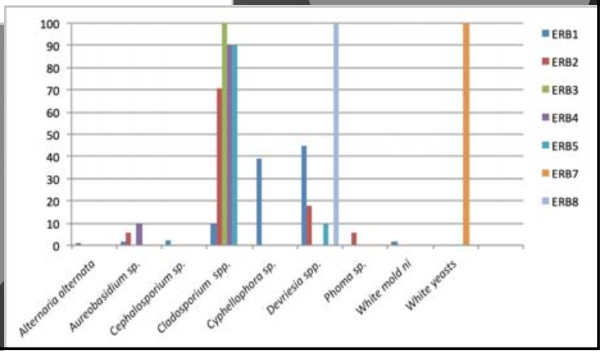
Sample	Bacteria (cfu/g)	Fungi (cfu/g)	Phototrophs (Presence/absence)
ERB1	$3.2 \cdot 10^5$	$2.0 \cdot 10^4$	++++++
ERB2	$6.5 \cdot 10^4$	$4.4 \cdot 10^6$	++++++
ERB3	$7.2, \cdot 10^5$	occasional	++
ERB4	$2.9 \cdot 10^6$	$3.0 \cdot 10^6$	-
ERB5	$8.0 \cdot 10^7$	occasional	++++
ERB6	$1.1 \cdot 10^8$	-	+
ERB7	$4.4 \cdot 10^7$	$1.0 \cdot 10^4$	-
ERB8	$2.1 \cdot 10^7$	occasional	++++

++++++ (very abundant growth);
++++ (abundant growth), ++ (discrete growth), + (scarce growth).

Results –before cleaning-



Frequencies of bacterial isolates from samples ERB taken prior any treatment and their taxonomic attribution



Frequency of fungi isolated from the different ERB samples prior any treatment and their taxonomic attribution.

Results - after cleaning -

. Summary of cultural analysis carried out after 1 months of biocide treatments

Sample	Bacteria cfu/cm^2	Fungi cfu/cm^2	Phototrophs Presence/absence
ERBD1	145	0	0
ERBD2	75	0	0
ERBD3	65	6	+
ERBD4	15	0	0
ERBD5	50	0	0

Results - after titania coating application -

Bacteria, fungi and phototrophs growing in BRII, DRBC e BG11 respectively after streaking on the surface 1 cm^2 of adhesive tape. Samples are divided on the basis of the treatment as shown in Plate Ic.

Samples	Treatment*	Bacteria	Fungi	Algae
ERBN1	B5%+Ag-TiO_2	-	+	++
ERBN2		-	+	-
ERBN3		++	+	+/-
ERBN8		+	+	-
ERBN4	B	++	+	+++
ERBN9		+	+	-/+
ERBN5	B10%+TiO_2	++	+	-/+
ERBN6	B5%+TiO_2	+	+	-
ERBN7	TiO_2	+/-	+	+

* = Binder; - = no growth; +/-= scarce growth; +=occasional growth; ++= discrete growth; +++= abundant growth.

Titanium dioxide: which future?

In May 2016 the -Agence nationale de sécurité sanitaire de l'alimentation, de l'environnement et du travail – has submitted a CLH proposal to ECHA to classify titanium dioxide as 1B with hazard statement H350i (May cause cancer by inhalation)

ANNEX 2 - COMMENTS AND RESPONSE TO COMMENTS ON CLH PROPOSAL ON TITANIUM DIOXIDE

Date	Country	Organisation	Type of Organisation	Comment number
01.07.2016	Denmark	National Research Centre for the Working Environment	BehalfOfAnOrganisation	429

Comment received

3) It is very useful that the conclusions explicitly stated that both bulk and nanoTiO2 are classified as Carc 1B
4) The literature search should cover the literature until april 2015. Here are a few studies that were published but are not included in the review that the authors may consider to include: Transcriptional profiling identifies physicochemical properties of nanomaterials that are determinants of the in vivo pulmonary response: 'Halappanavar S, Saber AT, Decan N, Jensen KA, Wu D, Jacobsen NR, Guo C, Rogowski J, Koponen IK, Levin M, Madsen AM, Atluri R, Snitka V, Birkedal RK, Rickerby D, Williams A, Wallin H, Yauk CL, Vogel U. Environ Mol Mutagen. 2015 Mar;56(2):245-64. doi: 10.1002/em.21936. Epub 2014 Dec 11. PMID: 25504612' and 'Pulmonary instillation of low doses of titanium dioxide nanoparticles in mice leads to particle retention and gene expression changes in the absence of inflammation. Husain M, Saber AT, Guo C, Jacobsen NR, Jensen KA, Yauk CL, Williams A, Vogel U, Wallin

as the same level of protection can be achieved by using more targeted directives on occupational safety and health (OSH) and effective and appropriate risk management

Conclusions

- In our case study, Nanosized titanium dioxide seems to have a bio-inhibition effect (mitigation)
- A longer period of monitoring is needed to understand the long-term behavior
- The use of these materials could be threatened by its classification by ECHA

Acknowledgments

POR Calabria FESR project "NANOPROTECH" (NANO PROtection Technology for Cultural Heritage)