Safer by molecular design in real industrial scenarios

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Sanowork

OPEN WORKSHOP

Operational occupational Risk Management Models and tools for MNMs in the industry

SENN2015

Scaffold nanoMICEX

istec

NanoSafety Cluster

OUTILINE

- SAFETY
- MOLECULAR DESIGN
- IMPLEMENTATION
WITHIN INDUSTRIAL CASE STUDIES
- SANOWORK RESULTS

SAFETY

SAFETY ISSUES APPLIED TO NANOMATERIALS.............

NANOSCALE REACTIVITY

SIZE ↔ SURFACE ↔ COMPOSITION

Quantum size effects,

Nanophase-heterogeneity determines the creation of an huge interface between nano-objects and the surrounding media

Low range order of crystallinity, surface defects

(non stoichiometric dissolution, redox reactivity, charge/electric properties, high surface energy)

POTENTIALLY HEALTH DANGEROUS EFFECTS

NMs APPLICATION

MOLECULAR DESIGN

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PREDICT AND CONTROL
RISK DETERMINANT PROPERTIES
DURING THE EARLY STAGE OF NANO-OBJECT DEVELOPMENT

PHYSICAL PROPERTIES
State of agglomeration
Degree of freedom for movement
Aspect ratio

CHEMICAL PROPERTIES
Redox reactivity
Dissolution behavior
Surface charge

EXPOSURE

EMISSIVITY
NANO-AEREOSOLIZATION
BIO-PERSISTENCY

RISK

BIOLOGICAL HAZARD

Oxidative stress
Cell injury
Cytotoxicity

Big challenge

High complexity

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SAFER BY MOLECULAR DESIGN SOLUTIONS

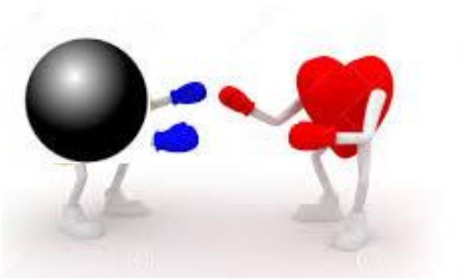
Wet dispersion state........
Matrix encapsulation

RELEASE

FATE, KINETICS

Homo- and heteroaggregation processes, depending on ENM properties and media components

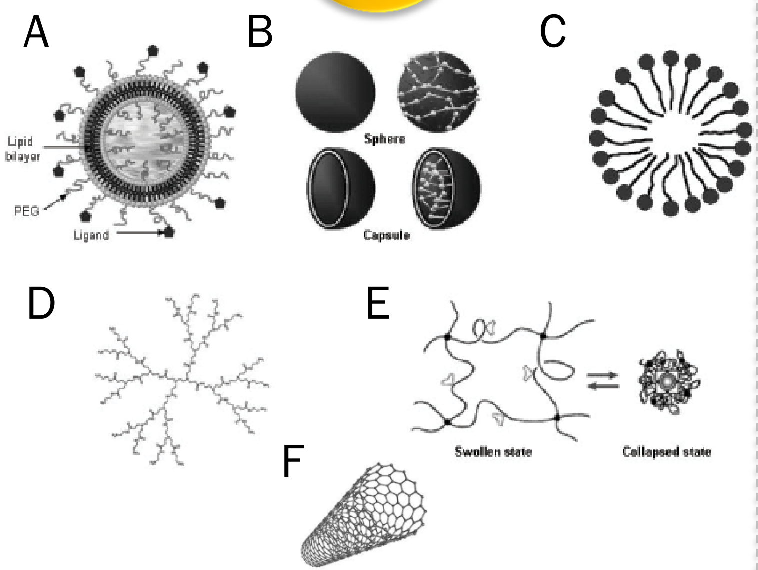
BIOLOGICAL REACTIVITY



Surface coatings are the primary dictators of many important nanomaterial properties, such as solubility, redox surface reactivity and macromolecule or cell surface interactions

1 COMPLEXITY

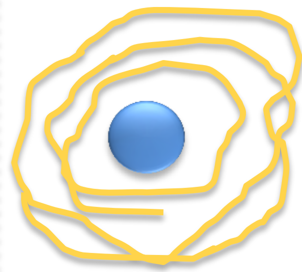
ORGANIC

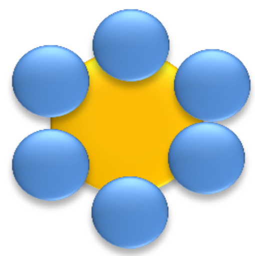


(A) liposomes; (B) polymer particles; (C) micelles; (D) dendrimers; (E) hydrogels; (F) carbonanotubes

Polymer colloids

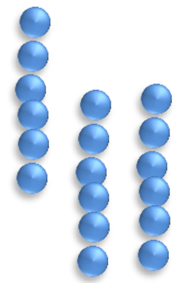
HYBRIDS



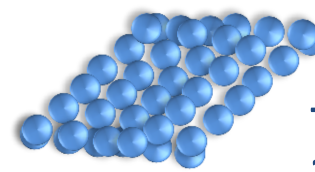


Nano composites

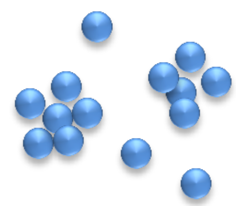
INORGANIC



Nanorods and nanowires
1D tructure
2 nano confinement



Thin film (plates)
2D structure
1 nano confinement



Nano particles (quantum dots, nanoclusters)
0D structure
3 nano confinement

Nanosize confined Metal, Metal Oxides

2 COMPLEXITY

KNOWLEDGE GAP

NANO OBJECTS

PROPERTIES

EXPOSURE HAZARD

OUTPUTS

IDENTIFICATION OF STRUCTURAL ALERTS

NANOMATERIALS CATEGORIZATION

TOX AND EXPOSURE PARADIGMS

PREDICTIVE MODELLING

COST / EFFECTIVENESS

LCA

3 COMPLEXITY

VALIDATION

RISK ASSESSMENT

ITS
(INTELLIGENT TESTING STRATEGY)
HARMONIZATION
REGULATORY ISSUES

PERFORMANCE ASSESSMENT

INTEGRATION OF MODIFIED MATERIALS INTO INDUSTRIAL MANUFACTURING SCENARIOS
EVALUATION OF PRODUCT AND PROCESS EFFICIENCY
INDUSTRIAL FEEDBACK

SANOWORK

- Start date: 1st March 2012
- Duration: 3 years
- EU contribution: €3,41 million
- Coordinator: A. L. Costa, CNR_ISTEC
- Consortium: 13 partners from 8 countries

Applied “safe nano design”concepts to nanomaterials risk management. Evaluated them

- by implementing exposure assessment methodologies in the workplaces
- by performing a risk analysis before and after the application of the proposed strategies
- by analyzing cost / benefit on the basis of the risk analysis results, NMs performances and extra steps cost evaluation

SANOWORK COMPANIES

Sanowork

COLOROBBIA

PlasmaChem

NANOMATERIALS

Elmarco NANO FOR LIFE

TECHNOLOGY

GEA-NIRO

PRODUCTS

Bayer Technology Services

LEITAT managing your technologies

Technological Center member of TECNIO

SEVENTH FRAMEWORK PROGRAMME

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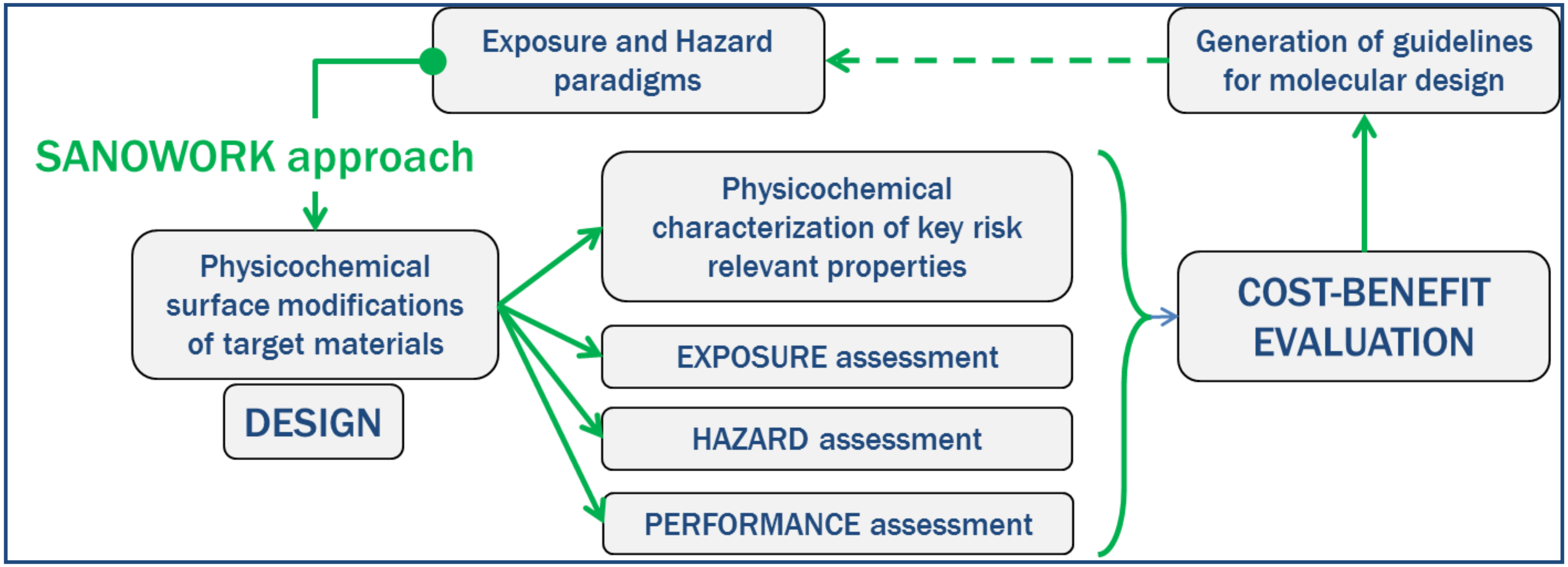
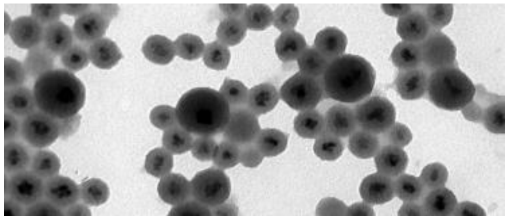
CONCEPTUAL FRAMEWORK

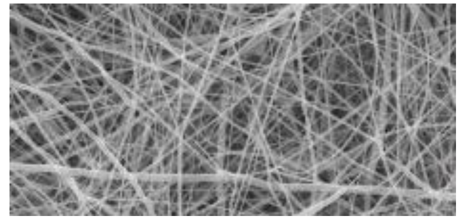


SANOWORK MATERIALS

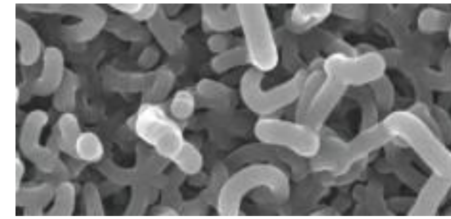
NANOPARTICLES



NANOFIBERS



NANOTUBES



ZrO_2 nanopowders

- additive in chemical industry
- raw ceramic material

TiO_2 nanosol

photocatalytic additive for ceramic (or textile) surfaces

Ag nanosol

antibacterial additive for ceramic surfaces

Polyamide nanofibers

nanostructured membranes for water depuration systems

TiO_2 nanofibers

photocatalytic component in solar cells

CNTs

additive in plastic industry

NMs with different

MORPHOLOGY (NPs, NFs, NTs)

CHEMISTRY (ZrO_2, TiO_2, Ag, Polyamide, C)

PHYSICAL STATE (Powder, Sol)

SANOWORK PROCESSING LINES

Sanowork

1

PlasmaChem

ZrO_2 NP Production Step

ZrO_2 NP Synthesis

ZrO_2 Crystallization

ZrO_2 Final Quality Control

Final ZrO_2 Product as powder or sol

2

GEA

ZrO_2 Ceramic Process Step

Spray Drying

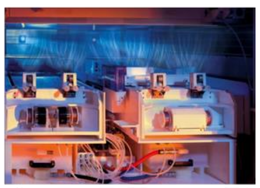
Green body

Cooking 1200°C

3

ELMARCO NANO FOR LIFE

PA Processing Step



PA electrospun

PA Manifacturing

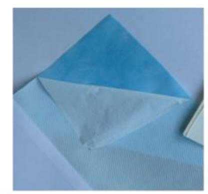
Final filter product

4

ELMARCO NANO FOR LIFE

TiO_2 Production Step

TiO_2 electrospun



NF peel-off

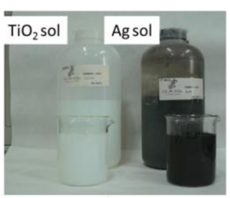
Calcination

Manufacturing

5

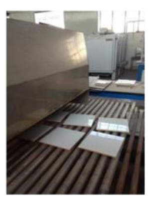
COLOROBBIA

Ag and TiO_2 Production Step



Ag and TiO_2 nanosol

Spray-coating



Curing

Quality check

6

LEITAT Technological Center managing your technologies member of TECNIO

CNTs Processing Step

Feed Preparation

Degassing molted polymers

Cleaning Process

SEVENTH FRAMEWORK PROGRAMME

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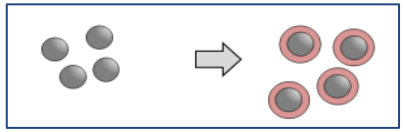
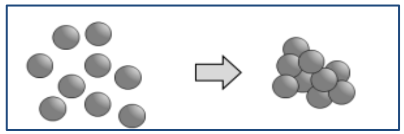
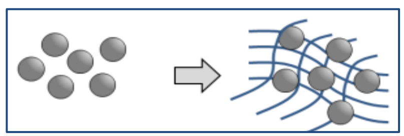
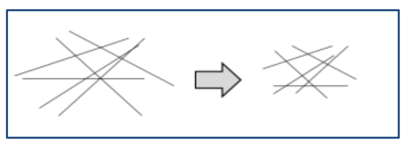
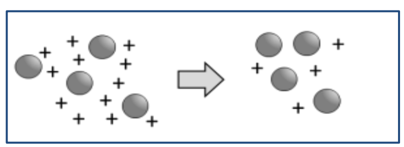
STRATEGIES ADDRESSED

PROPERTIES ADDRESSED AND SOLUTIONS PROVIDED		STRATEGIES DESCRIPTION
REDOX / SURFACE CHEMICAL REACTIVITY ***Protective layer*** • Inorganic coating (Silica) • Organic coating (Citrate)		***COATING*** with inert inorganic materials by heterocoagulation or chemical synthesis or with organic antioxisant nolecules
NANO-SIZE ***Agglomeration*** • Spray-drying • Freeze-drying • Colloidal destabilization		***'NANO' IN 'MICRO'*** forced agglomeration/aggregation, preserving nanoscale reactivity in a micron structure
NANO-SIZE ***Control free nanoparticles*** • Gelatine coating		***IMMOBILIZATION*** embedding nanoparticles in an inert organic matrix, easily removable after critical nano-manufacturing steps
ASPECT RATIO ***Decrease aspect ratio*** • Wet milling		***MILLING*** reduce and homogenize nanofibers length
FREE IONS ***Control free ions*** • Ultrafiltration		***PURIFICATION*** treatment applied to decrease the excess of free ions

RISK / PERFORMANCES EVALUATION

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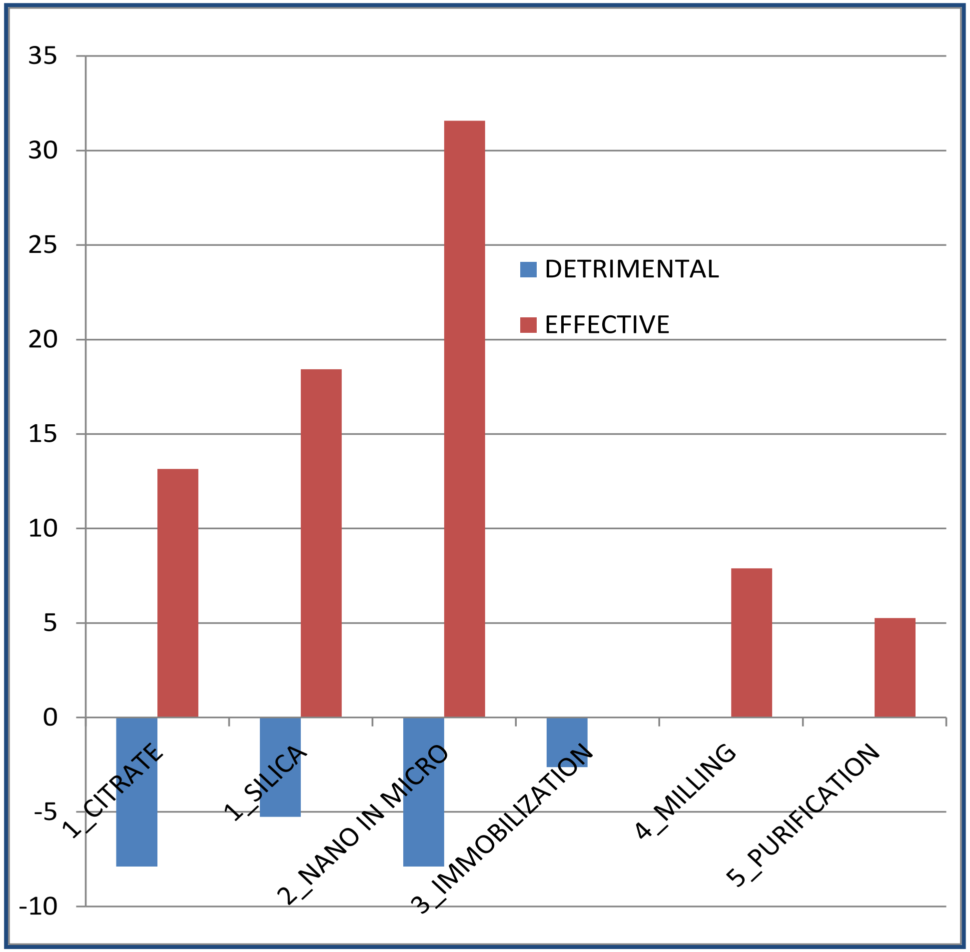
SAFETY BY DESIGN considering for each strategies the total amount of positive and detrimental effect due to their introduction and weighting for the total amount of experiments carried on



Nano in Micro *technologies (spray drying, spray-freeze granulation, forcing colloidal agglomeration) seem to be the most promising strategies for the control of emission/exposure potential,*

as well ***Silica Coating*** *is for the control and harmonization of surface chemistry*

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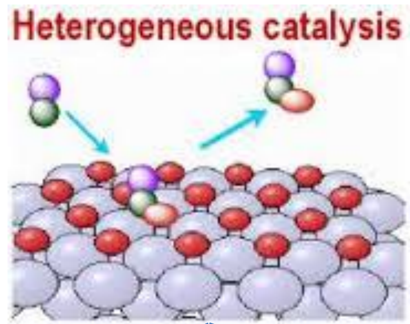
SEVENTH FRAMEWORK PROGRAMME

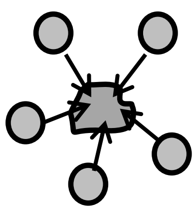
NANO IN MICRO TECHNOLOGIES

HETEROGENEOUS CATALYSIS



The catalyst is immobilized in a bulk reactive surface and can be easily recovered at the end, limiting its release in the environment and allowing the re-use

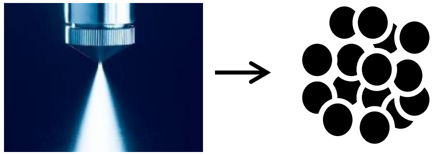
COLLOIDAL TECHNIQUE



Forced aggregation
(sedimentation, aggregation)

Preserving the primary nano-scale structure

PHYSICAL TECHNIQUE



Spray granulation
(spray-drying, spray-freeze granulation)

FORCING AGGREGATION

TO IMPROVE POWDER RECOVERY FROM WASTE WATER

Controlling environmental exposure

TO ALLOW POWDER RECYCLING AFTER RECOVERY

Improve process efficiency / sustainability

ZrO_2

Waste water...

Forced gelation by base addition

Wastes of ZrO_2 easily collected...

Dissolved in HCl or HNO_3 and hydrolized to produce fresh ZrO_2 powder

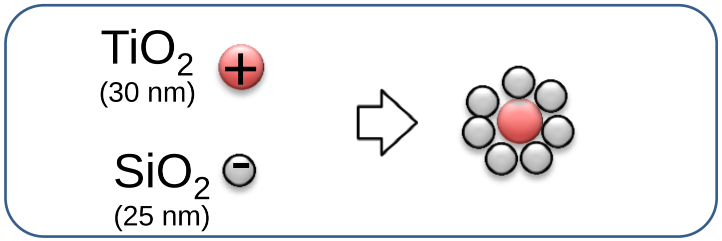
RESULTS

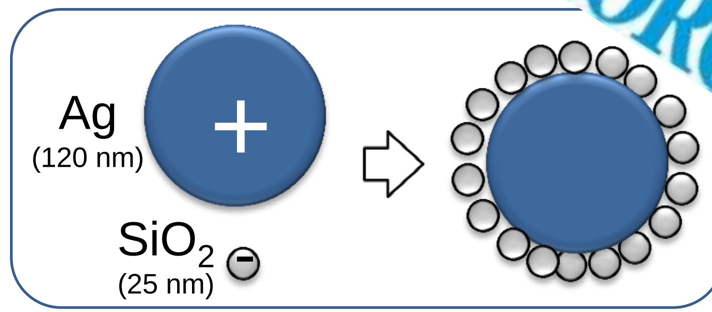
- ***Reduction of wastes quantity by ca. 99%*** *could be achieved*
- ***Quality*** *of the product manufactured from the* ***regenerated wastes*** *is comparable with the product manufactured by the original procedure*
- ***Reduction*** *of production self-costs* ***by 7%***

SILICA COATING

COLLOIDAL

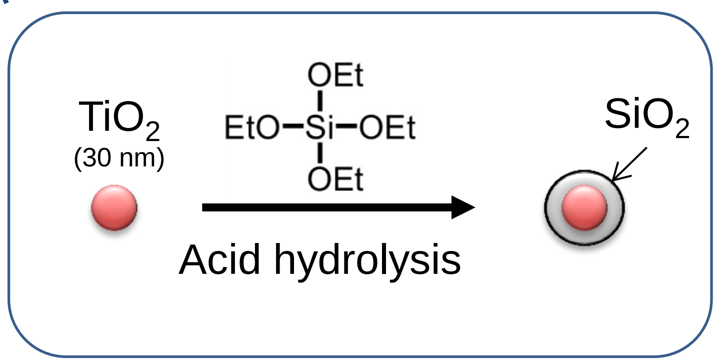
MATRIX ENCAPSULATION

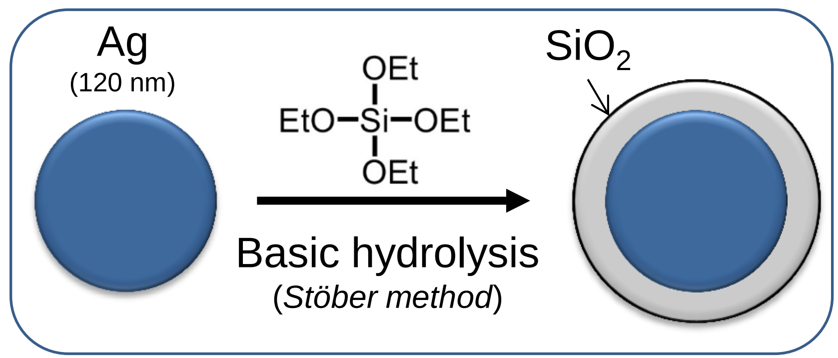




CHEMICAL

CORE SHELL ENCAPSULATION





COST / BENEFIT EVALUATION

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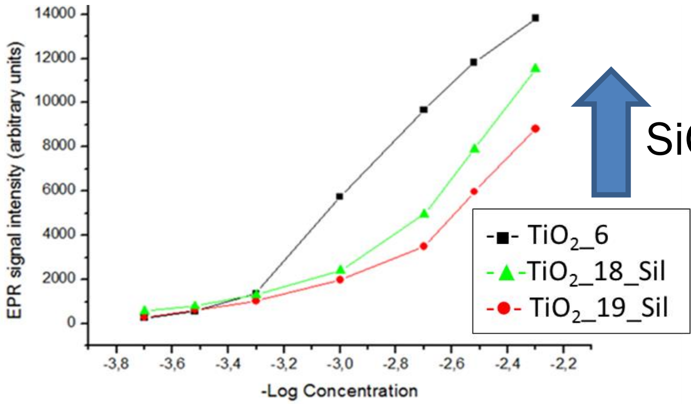
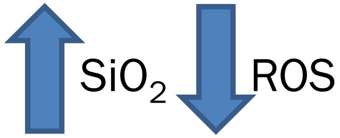
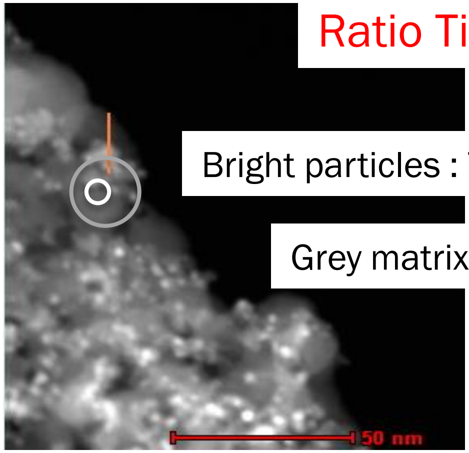
ROS production

EPR signal vs total solid conc, **not normalized for the content of TiO_2**

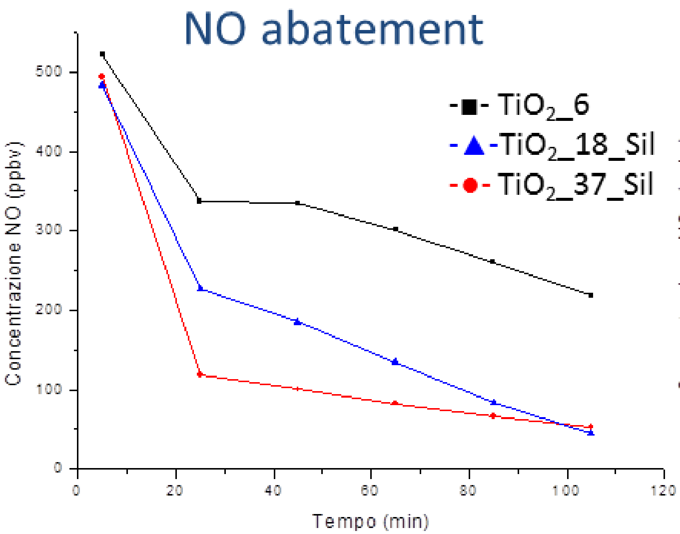


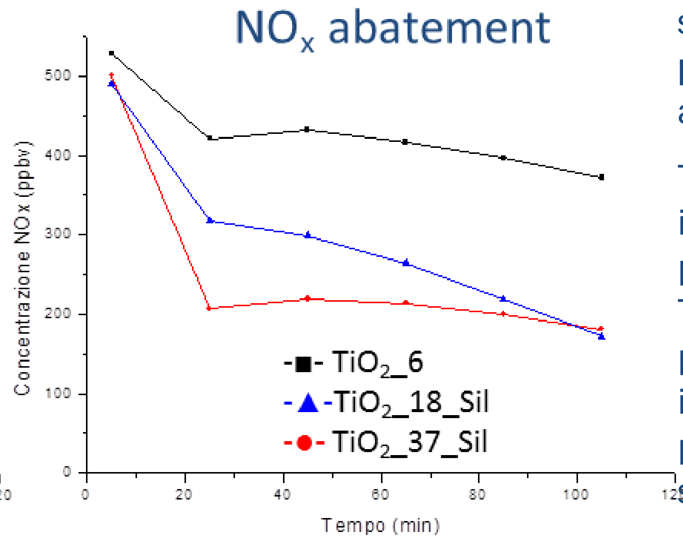


Ratio TiO_2:SiO_2 1:3



Performance evaluation





Silica modified TiO_2 samples showed an **improvement of photocatalytic performance** in all cases!!!

The unexpected and very interesting result is that it is possible to dilute the amount of TiO2 with silica, decreasing the production of ROS, but improving the photocatalytic performances of pristine sample.

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CONCLUSIONS

- *“ADDRESSING SAFETY ISSUES AT THE EARLY DESIGN STAGE OF THE PRODUCT OPEN NEW CHALLENGES TOWARDS THE DEVELOPMENT AND PROMOTION OF NENOMATERIALS THAT SATISFY PERFORMANCE AND SAFETY REQUIREMENTS*

- *THE FP7 COLLABORATIVE PROJECT SANOWORK: NMP4-SL-2012-280716, DEVELOPED «DESIGN OPTION» BASED RISK REMEDIATION STRATEGIES AND INTEGRATE THEM WITHIN INDUSTRIAL PROCESSING LINES*

- *IMPORTANT OUTPUTS WERE ACHIEVED:*
  - *SOUND AND PRACTICAL HAZARD ASSESSMENT COUPLED WITH THE IDENTIFICATION OF STRUCTURAL ALERTS*
  - *THE ESTIMATION OF THE EXPOSURE POTENTIAL IN REAL INDUSTRIAL SCENARIOS*
  - *THE EVALUATION OF COST / BENEFIT IN TERMS OF PERFORMANCE ASSESSMENT, COST ESTIMATION AND RISK REDUCTION OF THE PROPOSED SOLUUTIONS*
  - *THE IDENTIFICATION OF MOST PROMISING SAFETY BY MOLECULAR DESIGN STRATEGIES TO BE APPLIED AT THE EARLY STAGE OF NANO-PRODUCT DEVELOPMENT, IN RELATION TO SPECIFIC RISK DETERMINANT CHARACTERISTICS*

SANOWORK LESSON: FUTURE PROSPECTIVES

Sanowork

SUN

WP 7 safe production, handling and disposal

GUIDELINES FOR NEW AND SUSTAINABLE RMS

...Future calls ?

Enforce "Safer by design" approach

NEEDS

Wet state characterization in environmental or biological relevant media

Modelling in support to design

Categorization, identification of key risk relevant factors that allow a quick identification, development and "validation" design solutions

A. L. Costa, "A Rational Approach for the Safe Design of Nanomaterial", Nanotoxicology: Progress toward Nanomedicine, Second Edition, March 3, 2014 by CRC Press Content, Editor(s): Nancy A. Monteiro-Riviere; C. Lang Tran (2014)

SEVENTH FRAMEWORK PROGRAMME
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SANOWORK CONSORTIUM

Paris, 13-14 March 2014, 24-Months-Meeting

Thank you very much for your attention!