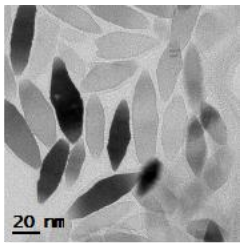
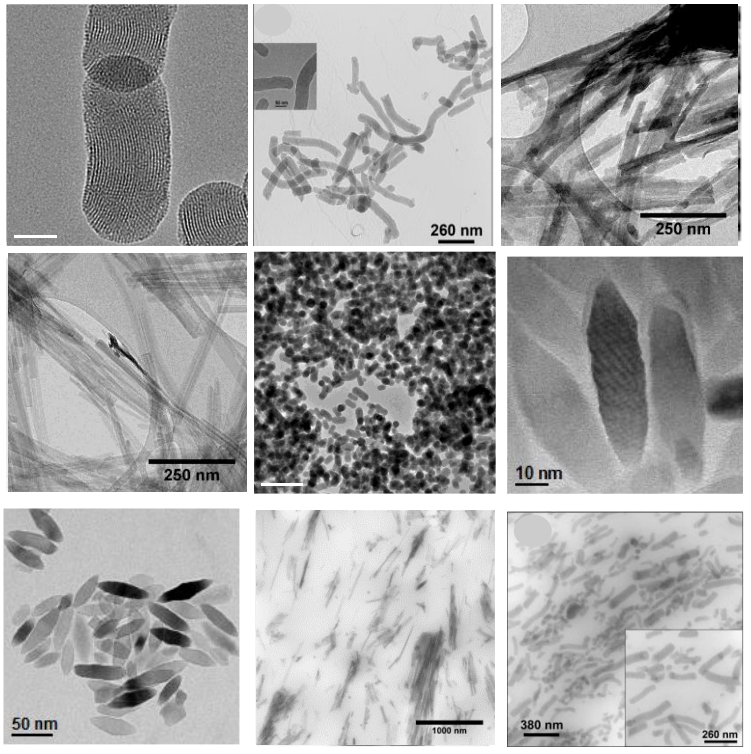
“Chemistry of inorganic and hybrid materials for energy saving and sustainability”

Roberto Scotti
Massimiliano D’Arienzo
Barbara Di Credico
Roberto Nisticò
Silvia Mostoni





NanoMat@Lab
Unimib

Follow us!
NanoMat-Lab

Industrial Collaborations: Pirelli Tyres, SAES-Getters, RSE
Academic Collaborations: University of Trento (NMR facility), CNR of Genova (TEM of nanocomposites); University of Venezia (TEM of NPs)

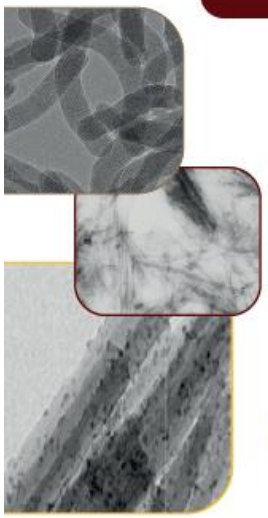
The NanoMat@Lab Unimib aims at the synthesis by soft-chemistry and at the characterization of inorganic pure and hybrid materials for energy saving

Shape and Controlled Anisotropic NPs (TiO_2, SiO_2, SnO_2, ZnO, CuO)

2D Layered Nanomaterials (MoS_2, WS_2,) **and Clays** (e.g. sepiolite fibers)

Poly Silsesquioxanes (PSQ) Molecules

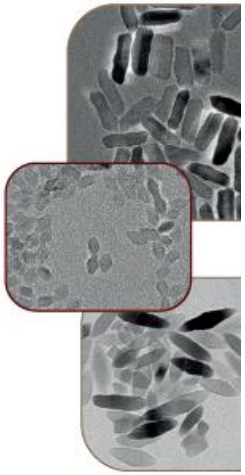
Selected Polymers: thermoplastics, elastomers & thermosettings



Material Preparation by Colloidal Methodes
(furnaces, autoclaves, dip-coating, spin-coating)

Structural & Morphological Characterization
(XRD, DLS, SEM, TGA-MS, ESR spectroscopy)

Functional Characterization
(TOC analyzer, DMA, Electrochemical Characterizations)



Application 1 Photocalytic and Catalytic Materials

Application 2 Polymer Nanocomposites for tires

Application 3: Materials for batteries and fuel cells

Application 4: multifunctional polymer composites

Application 5: recycling and re-use of oxide materials

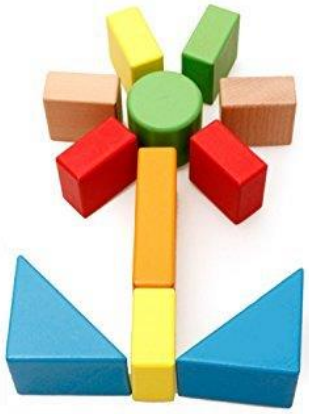
Application 6: Photodynamic therapy

Application 7: Magnetic nanomaterials for environmental remediation

Our approach:

…shape, size and surface control

…different final objects with different structure

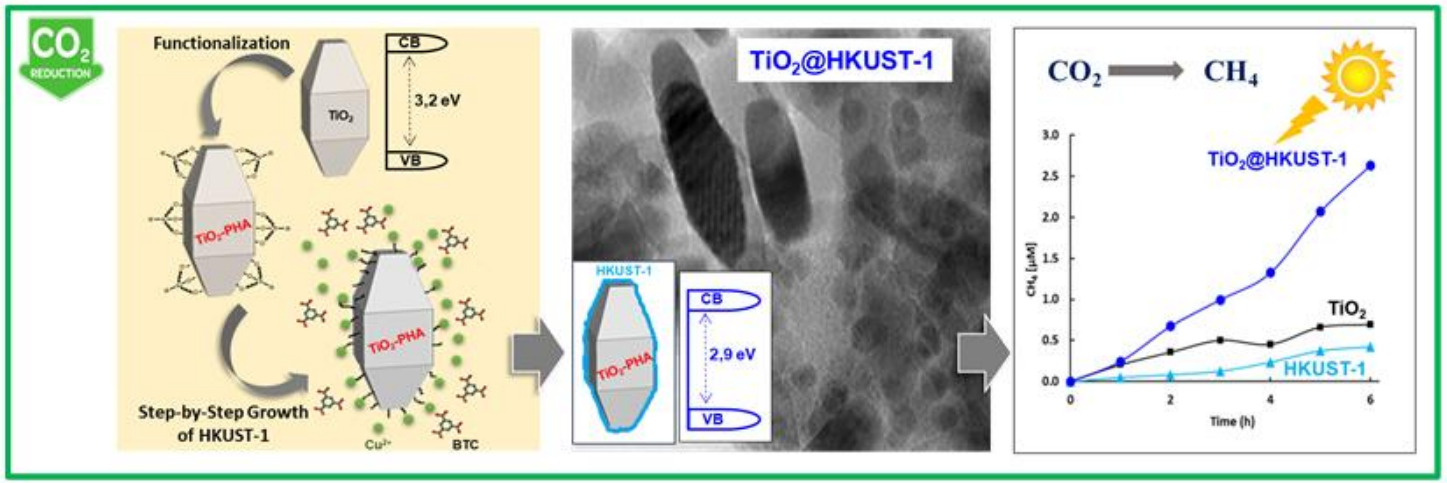


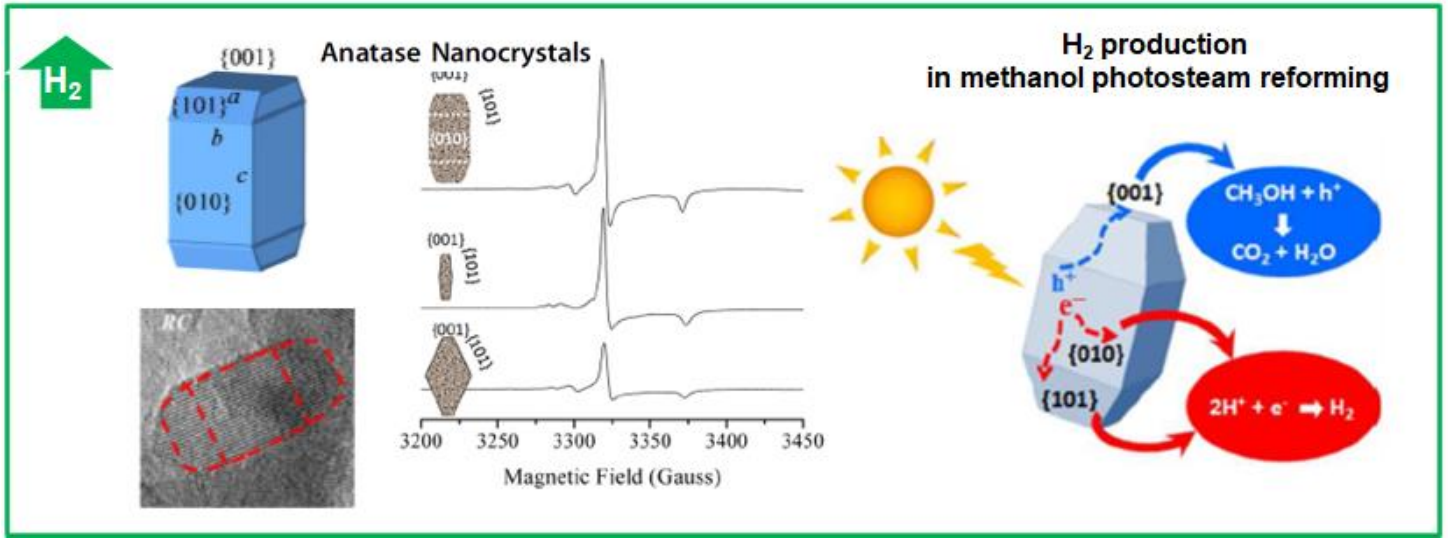
…enclose them in other materials, making sure they are suitable (i.e. organic/inorganic polymers)

…impart peculiar properties, taking care of the interfaces (study of hybrid interfaces)

Application 1
Photocalytic and Catalytic Materials

Preparation of TiO_2 NPs with controlled morphology and surface functionalization for catalysis & photocatalysis





JACS **2011**, 133**,** 17652

Applied Cat. B: Environ. **2011**, 104, 282

JPCC **2015**, 119, 12385-12393.

Appl. Catal. B, **2013**, 130, 239

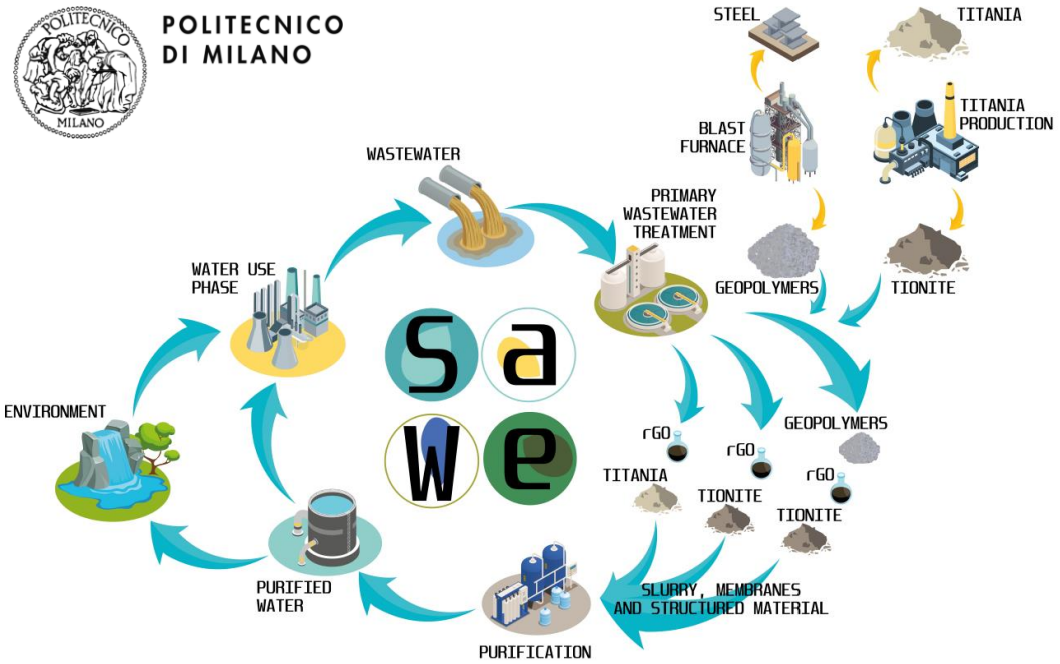
International Journal of Photoenergy, 1-14, (**2015**)

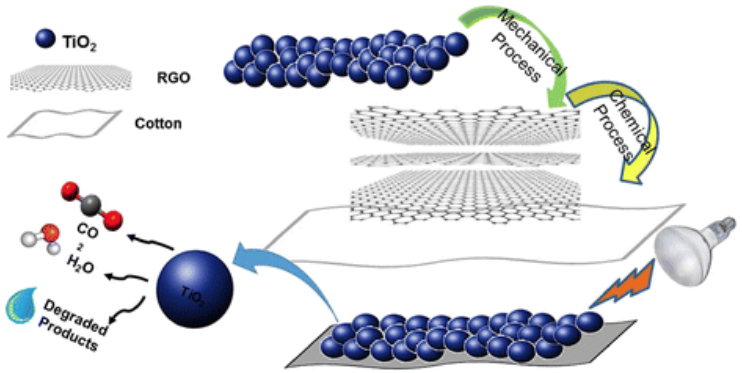
Catalysts **2018**, 8, 353

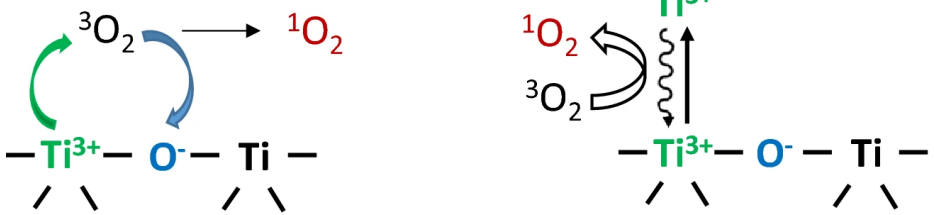
Application 1
Photocalytic and Catalytic Materials

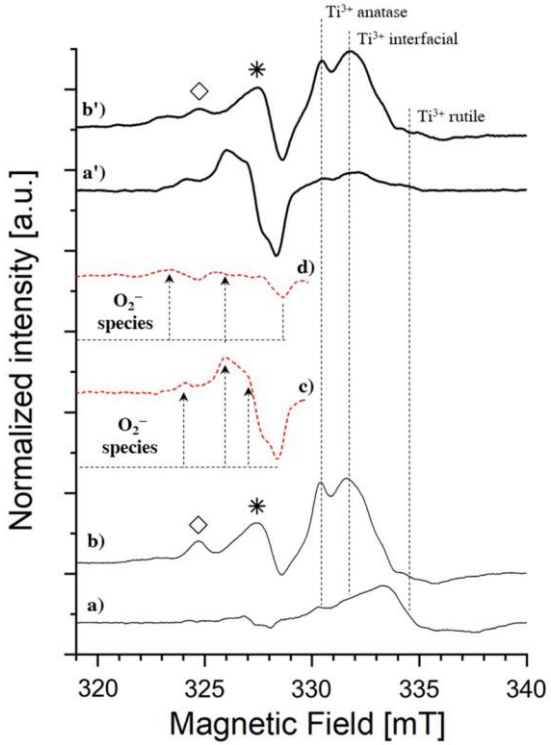
Preparation of TiO_2 NPs with controlled morphology and surface functionalization for catalysis & photocatalysis

POLITECNICO DI MILANO







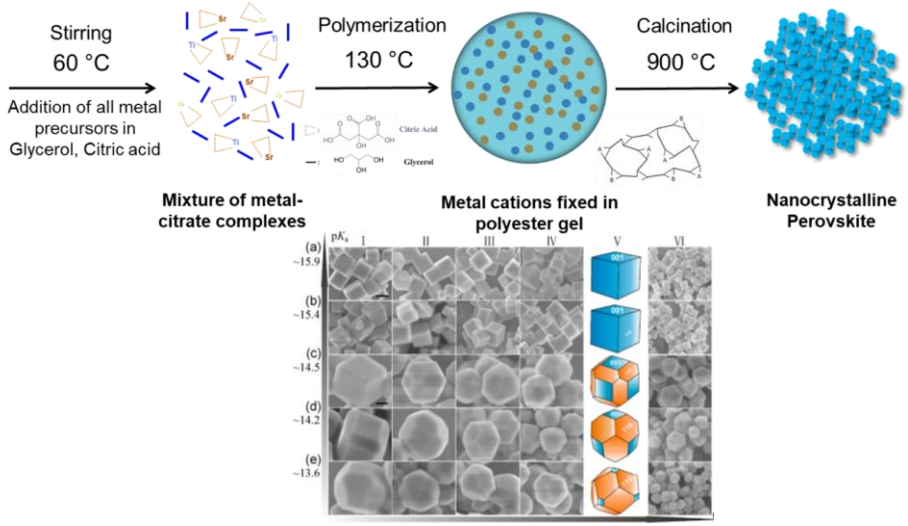


Topics in Current Chemistry **2022,** *380*, 2

Application 1
Photocalytic and Catalytic Materials

Design and characterization of $SrTiO_3$ materials with in-situ exsolved transition metal NPs for catalytic applications

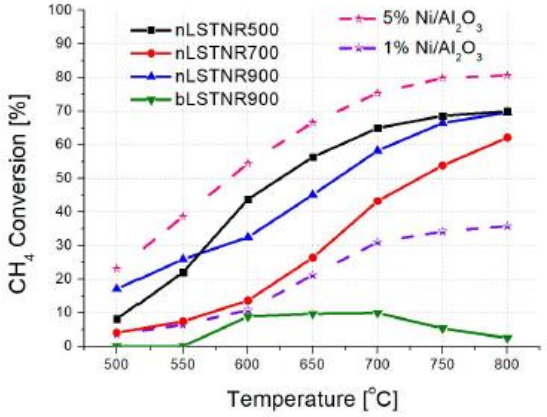
Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

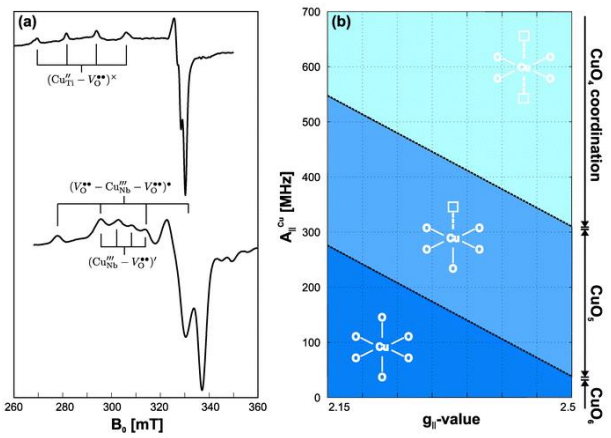


Tune the morphology to design the desired nanoparticles and to tailor exsolution on different facets

Biogas dry reforming applications

$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$



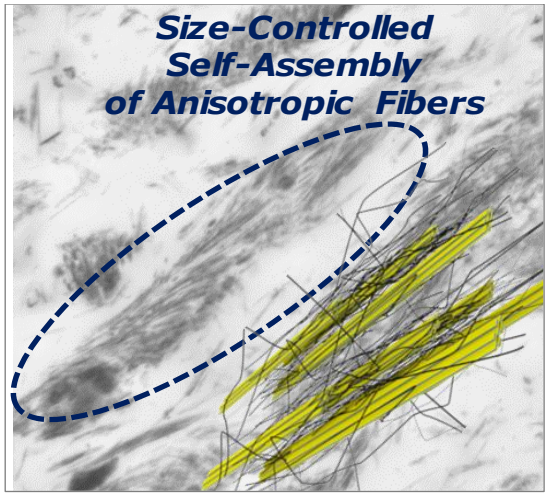


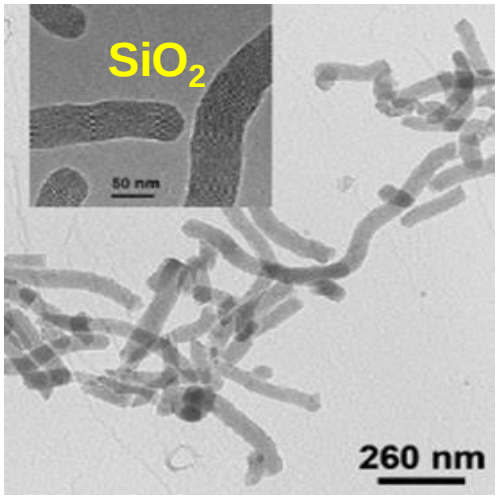
- **ESR for detecting paramagnetic metals**
- Informations about metal states and difects in the lattice
- Possibility to **follow the generation of defects and distinguish the coordination and geometry of metals**
- ***Quasi in-situ* analysis of the exsolution process**

Application 2
Polymer Nanocomposites for tires

Inorganic filler systems for tires applications

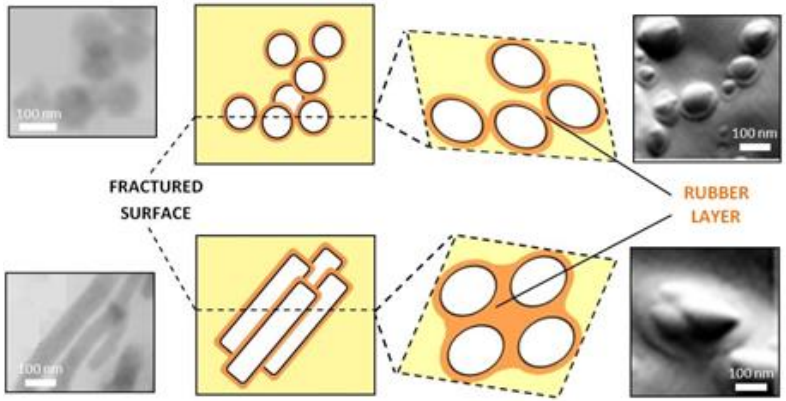
- Preparation and functionalization of SiO_2
- Modification and functionalization of clays

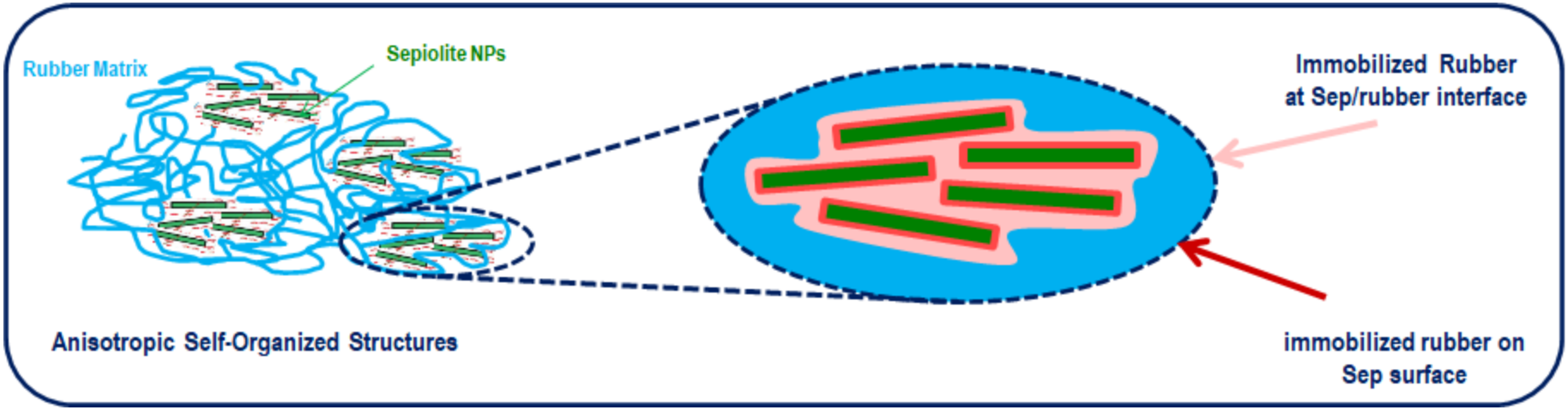




Applied Clay Science, **2018**, 152, 51-64 *Nanomaterials* **2019**, 9, 486

Nanomaterials **2019**, 9, 46 *Applied Clay Science*, **2021**, accepted

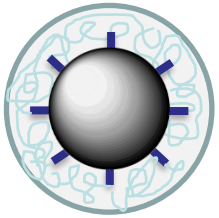




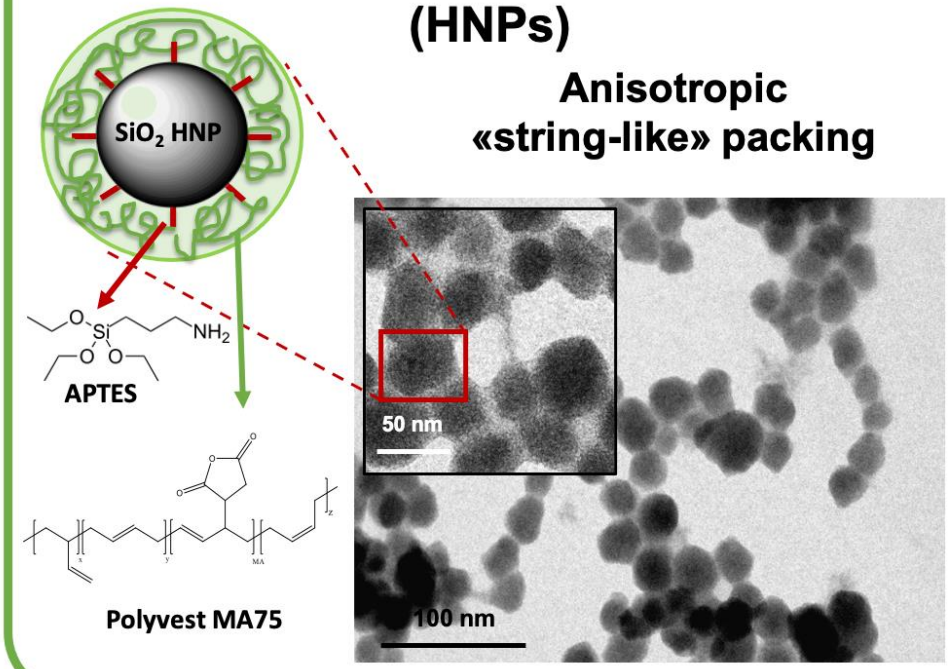
Application 2
Polymer Nanocomposites for tires

Inorganic filler systems for tires applications

Hairy nano-particles HNPs (polymer-grafted NPs), dispersed in the homopolymer matrix, able to self-assemble in higher order **anisotropic structures**

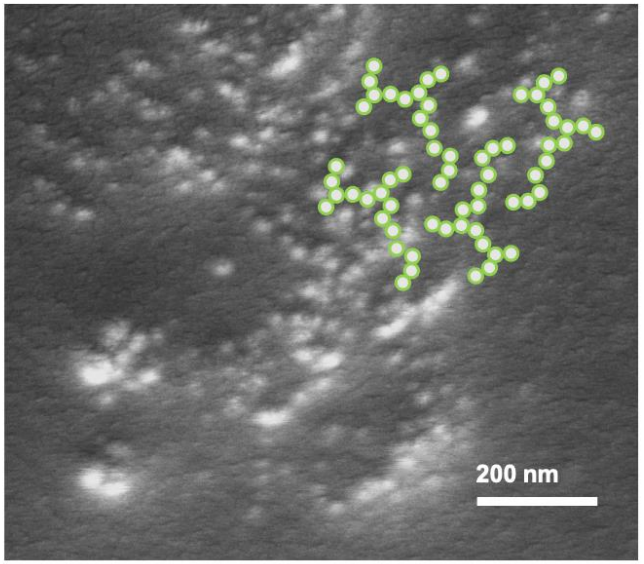


Synthesis of SiO_2 Hairy Nanoparticles (HNPs)



Polymer nanocomposite

Self-assembly of SiO_2 HNPs



Soft Matter **2021**, 17, 9434

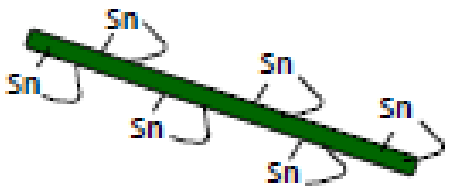
Application 2
Polymer Nanocomposites for tires

Inorganic fillers and vulcanizing systems for tires applications

From anisotropic silicate particles by sol-gel route and modified Sepiolite to SmartNet SILICA™

PIRELLI

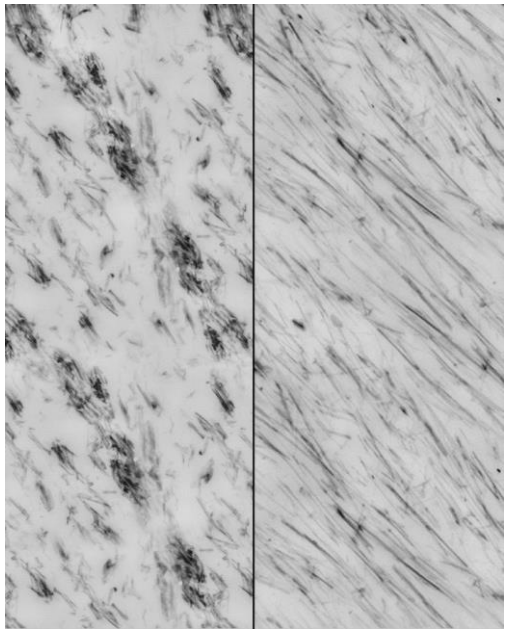
SMARTNET SILICA™



- Elongated primary particle shape which promised higher reinforcement
- Surface chemistry determines low hysteresis

https://velo.pirelli.com/it/it/tecnologia-pirelli-p-zero-velo

Anisotropic nanoparticles self-organize in domains



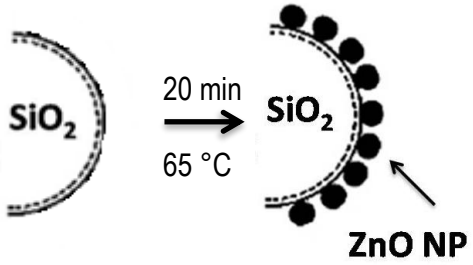
	G'(9%) (MPa)	G'(0.5)-G'(10) (MPa)	TanDelta (9%)*
Silica	0.834	0.252	0.081
SmartNetSilica	0.854	0.077	0.052

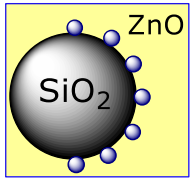
Application 2
Polymer Nanocomposites for tires

SiO_2@ZnO vulcanizing systems for tires applications

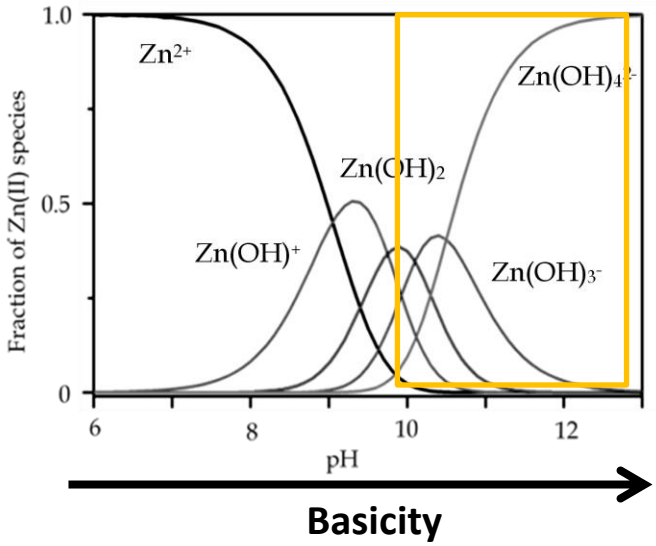
- Hydrolysis and condensation of $Zn(CH_3COO)_2 \cdot 2H_2O$ on silica surface

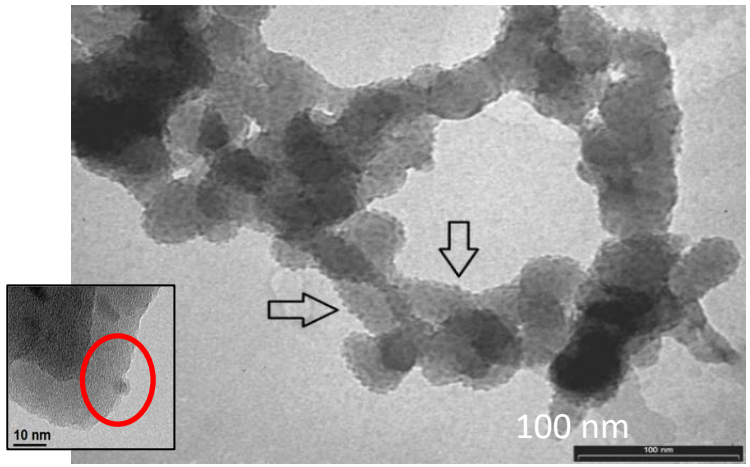
- SiO_2 nanoparticles (Rhodia1165 MP)
- *Precursor*: $Zn(CH_3COO)_2 \cdot 2H_2O$
- *Solvent*: CH_3CH_2OH
- *Base*: NaOH





- ZnO NPs grow on silica from a stable colloidal solution
- $Zn(OH)_n^{2-n}$ interact with the silanol groups at the surface of silica particles and induce the growth of ZnO NPs





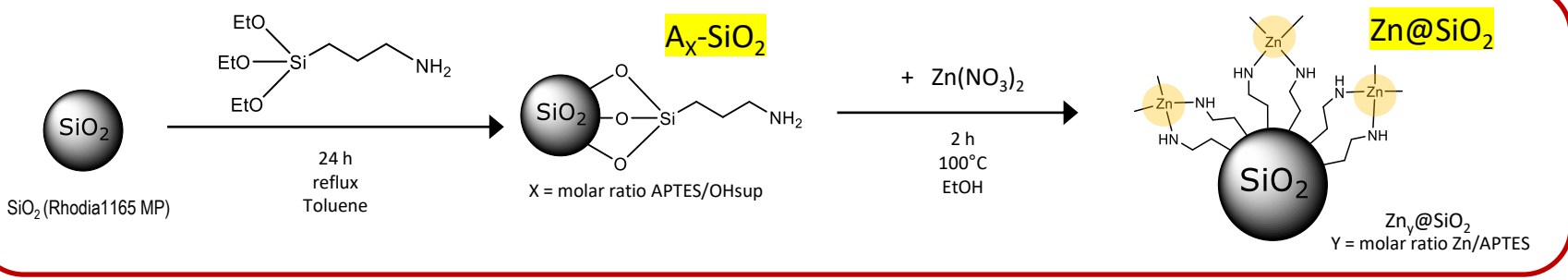
ZnO-7.7 SiO_2

Chem. Eng. J. **2015**, 275, 245

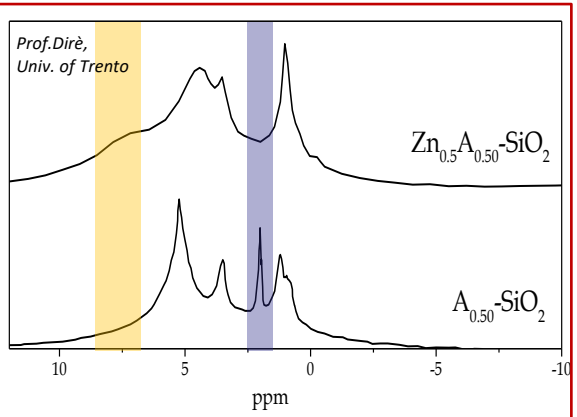
European Polymer Journal, **2017**, 93, 63

Application 2
Polymer Nanocomposites for tires

SiO_2@ZnO vulcanizing systems for tires applications



Solid state NMR ^1H single pulse



- 1.9 ppm: -NH_2 group
- Shift to 7.3 ppm due to **Zn^{2+} interaction** with the amino group

Sun Ha Kim et al., Korean Chem. Soc., 2011, 32 (10), 3644-3649

ICP-OES (Optical Emission Spectroscopy)

Sample	n_{Zn}/n_{APTES}	%wt Zn (measured)
$Zn_YA_{0.33}$-SiO_2	0.5	2.2 ± 0.2
	1.0	
	2.0	
$Zn_YA_{0.50}$-SiO_2	0.5	3.1 ± 0.2
	1.0	
	2.0	

Quantification of zinc

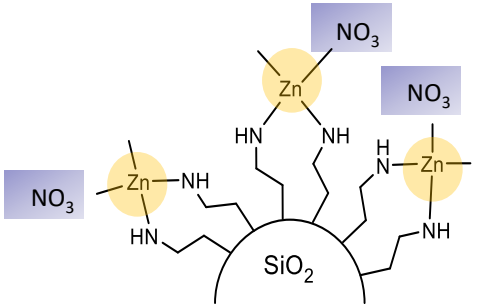
- % Zn wt **depends** on the amount of APTES
- **Zn atoms : linked APTES molecules: 1:2**

XPS (X-ray Photoelectron Spectroscopy)

Sample	NH/Zn ratio	Zn/NO_3 ratio
$Zn_{0.5}A_{0.50}$-SiO_2	1.7	1.5

Prof. L.Armelao, Univ. of Padova

- Single-site zinc centres anchored on SiO_2
- Coordination Zn:APTES 1:2
- % Zn dependent on the surface functionalization
- Positions around Zn centres coordinated with NO_3^-, OH^- or H_2O and available to react with curatives

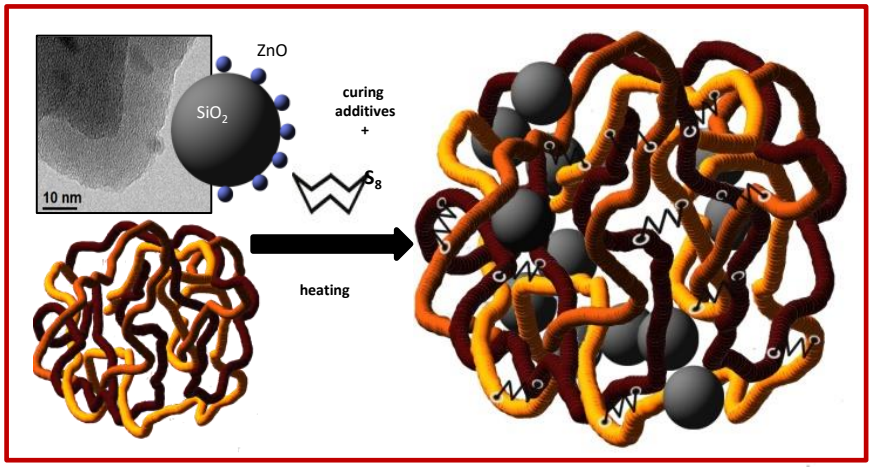


Industrial and Engineering Chemistry Research **2021,** 60, 10180

Application 2
Polymer Nanocomposites for tires

SiO_2@ZnO vulcanizing systems for tires applications

EIT KIC Raw Materials – Up-Scaling project
18145 - SAFE-VULCA (2019)
Safer reduction of ZnO amount in rubber vulcanization process
Roberto Scotti - Project coordinator
Università degli studi di Milano-Bicocca (UNIMIB)

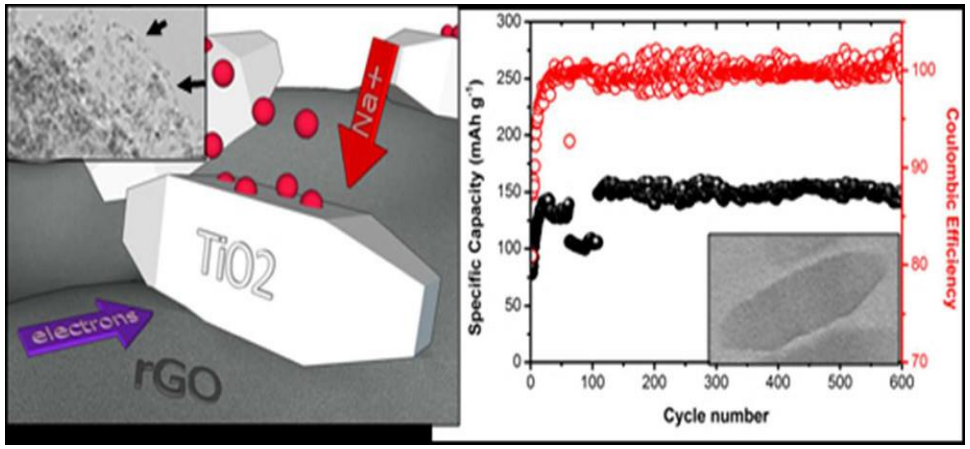


MONOLITHOS CATALYSTS - RECYCLING - INNOVATION
cea
Fraunhofer ISC
Radboud Universiteit
UNIVERSITÀ DEGLI STUDI DI MILANO BICOCCA
PIRELLI

Application 3: Materials for batteries and fuel cells

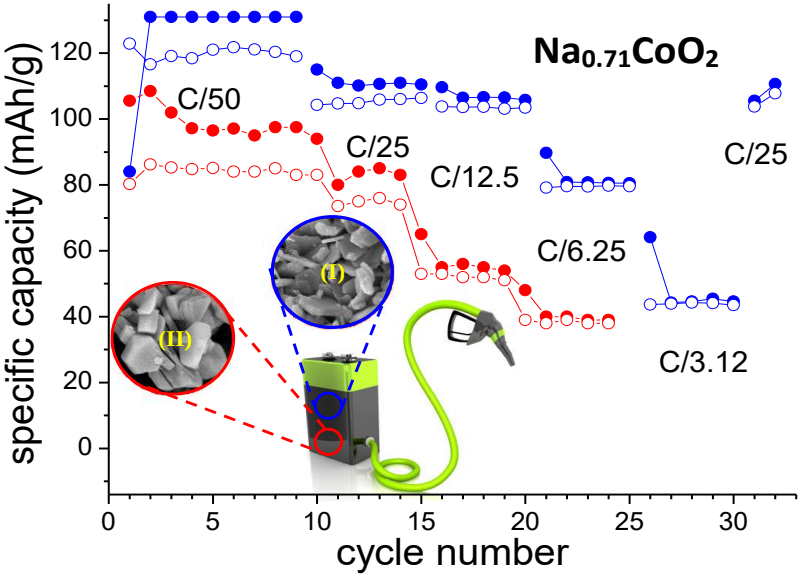
Preparation of metal oxide NPs with controlled morphology and surface functionalization for application in Li/Na batteries

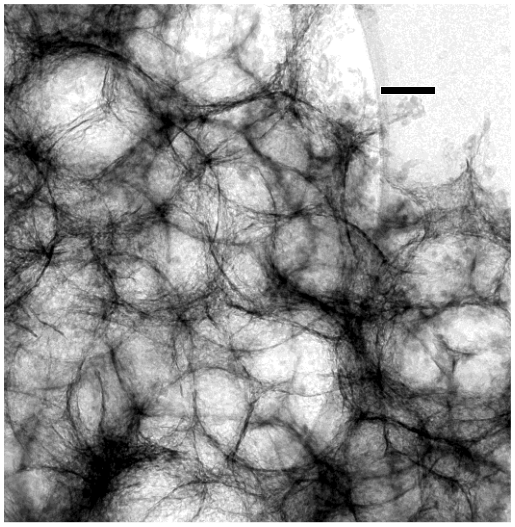
In collaboration with prof. Riccardo Ruffo



- soft-chemistry synthesis and surface functionalization of SiO_2, TiO_2, MoO_3
- Electrochemical characterization

PCCP **2012**, 14, 5945
Nano letters **2017**, 17, 992
Electrochimica Acta **2021**, submitted

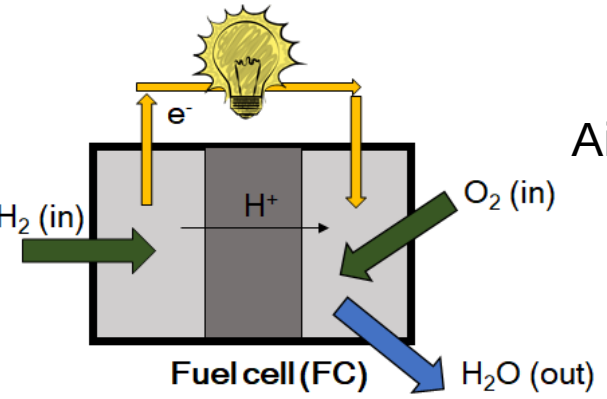




Application 3: Materials for batteries and fuel cells

Preparation of carbon based materials with controlled morphology and surface functionalization for application in fuel cells

In collaboration with dott. Carlo Santoro



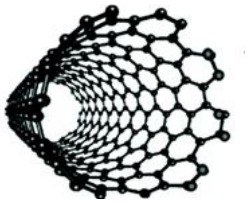
Aim: development of new materials as Electrocatalysts (ECs)

Engineering performant 3D porous structure + exposed metal sites

✗ Reduce the use of Pt/C → so far the most efficient but high costs and low stability

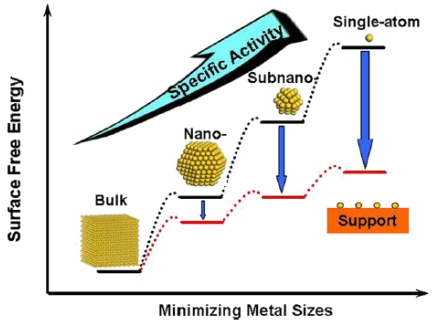
✓ **Platinum free ECs**
Single transition metal centers
(pyrolytic methods)

Carbon supports with porous structure

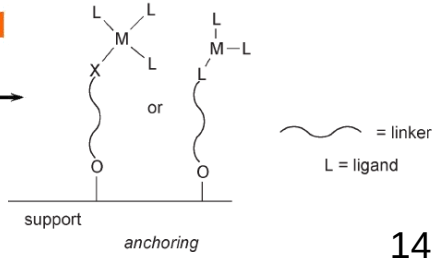

Carbon nanotubes CNTs


Mesoporous carbon

Single metal sites through soft chemistry techniques

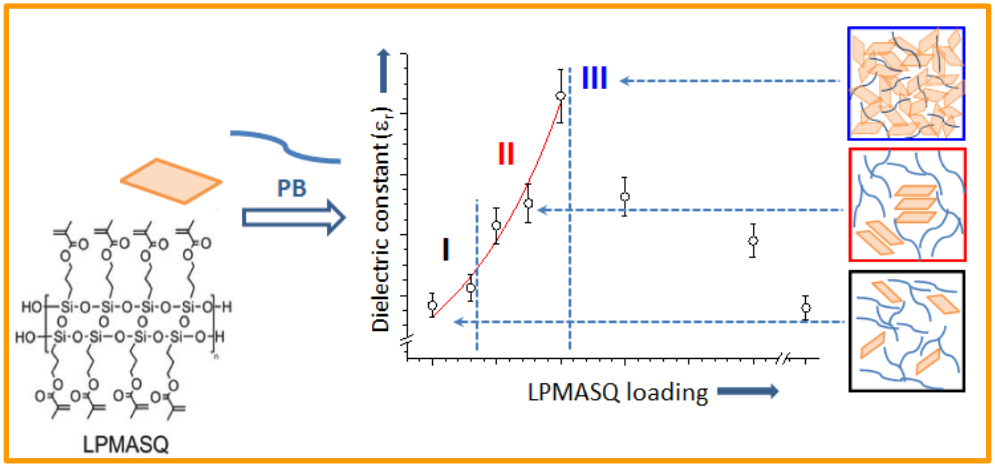


M- FG-C
M = Fe, Co, …
FG = functional group



Application 4: Multifunctional polymer composites

Exploiting polysilsesquioxanes for polymer composites



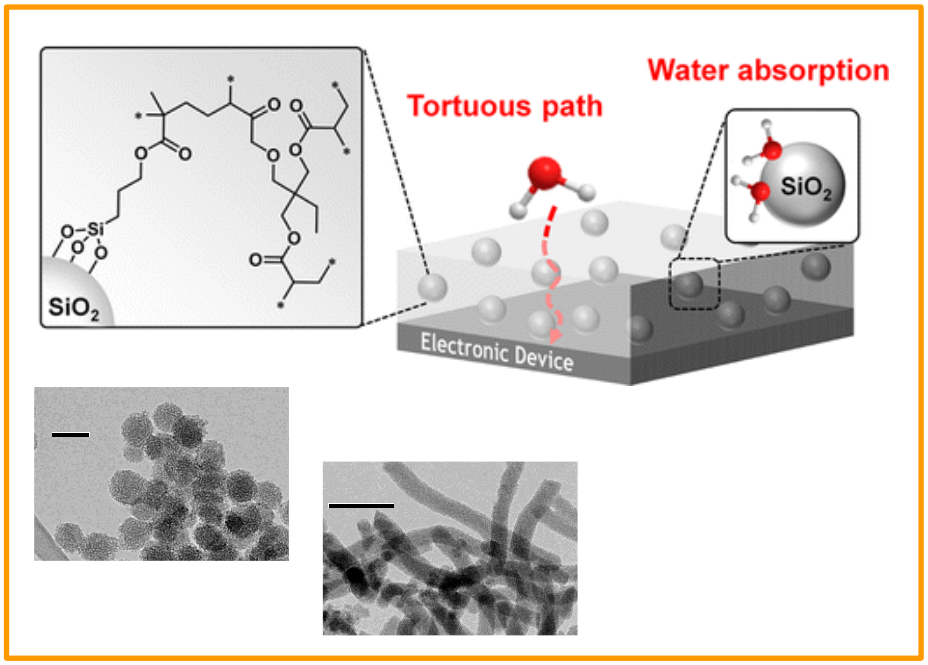
- Preparation of polysilsesquioxanes with tailored structure and functionalities (ladder-like and POSS)
- Study of the hybrid interfaces

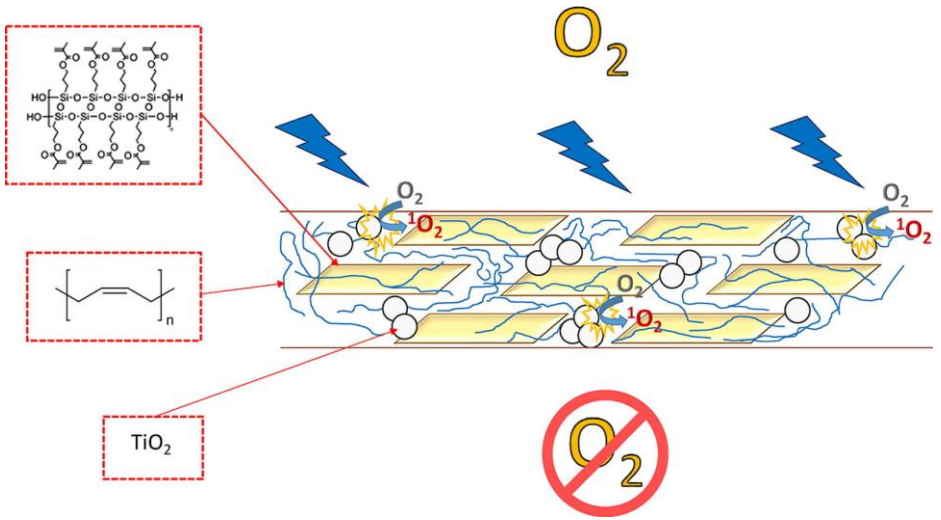
Journal of colloid and interface science **2018**, 512, 609

ACS Applied Nano Materials **2018**, 1, 3817

Coatings **2020**, 10, 913

Chemical Engineering Journal **2021**, 417, 129135



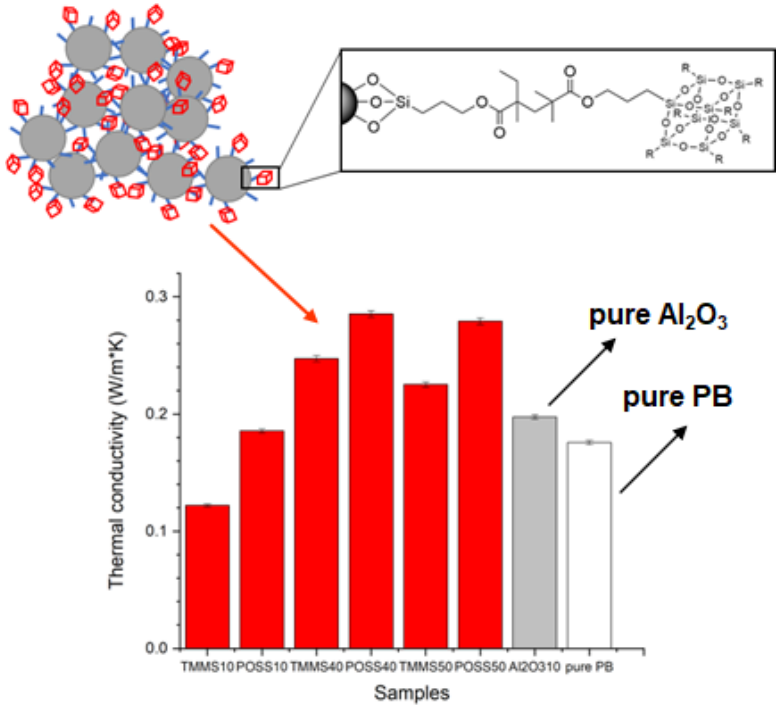


Application 4: Multifunctional polymer composites

Thermal conductive & self-healing nanocomposites

Al_2O_3@POSS

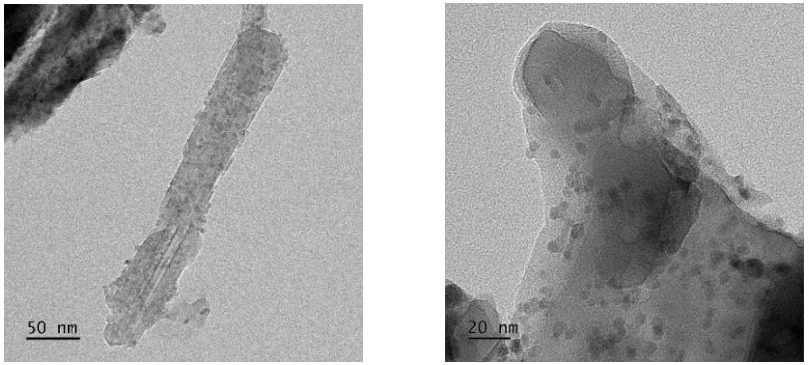
- Exploiting the **methacryl groups of the POSS for the self healing** of acrylic elastomers mediated by hydrogen bond between carbonyl and hydroxyl groups

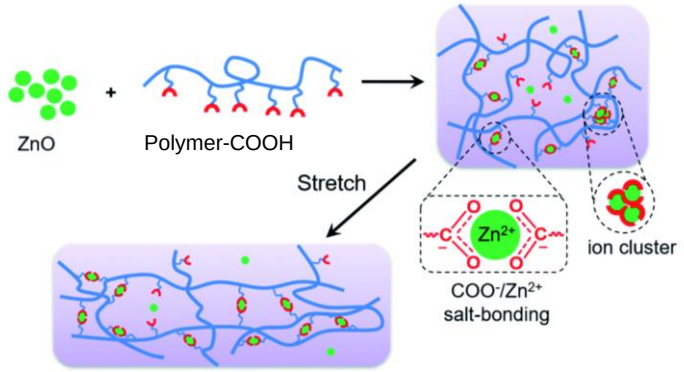


- *Activities in collaboration with* CSIC Madrid
  Consejo Superior de Investigaciones Científicas

Al_2O_3@ZnO & metal complex

- ZnO has been reported to form dynamic ionic crosslinks in carboxylated polymers. **Al_2O_3@ZnO** could be used to produce self healing **XNBR** nanocomposite.

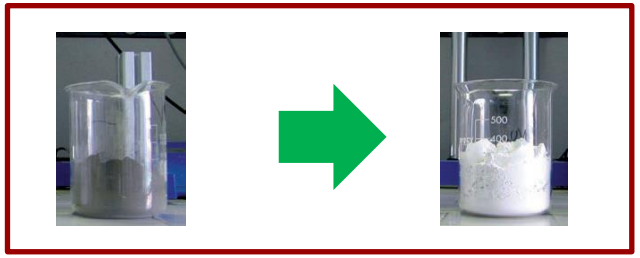




Application 5: Recycling & Re-use of oxide materials

Recovering of waste silica and re-introduction in the value chain

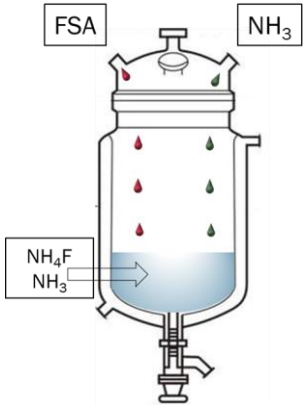
Reuse of silica as reinforcing filler for rubber from hexafluorosilicic acids, secondary product of the phosphate production



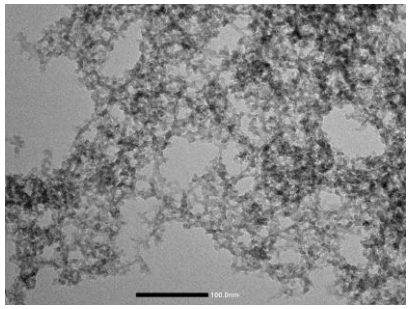
Silica preparation :

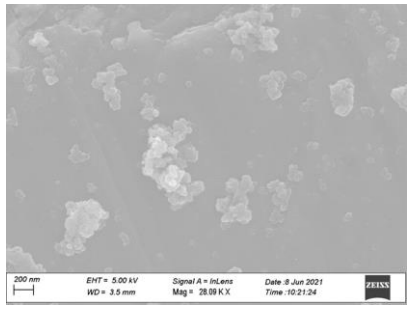
$$H_2SiF_6 + 2\,NH_4OH \rightarrow (NH_4)_2SiF_6 + 2H_2O$$

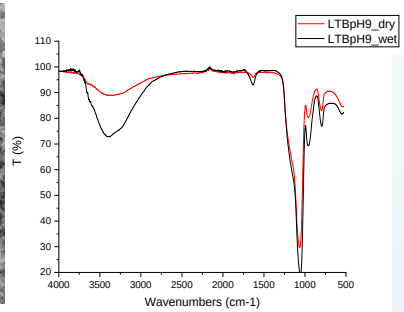
$$(NH_4)_2SiF_6 + 4\,NH_4OH \rightarrow \mathbf{SiO_2} + 6NH_4F + 2H_2O$$

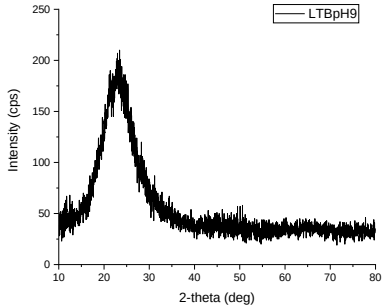


Fluidized bed Drying





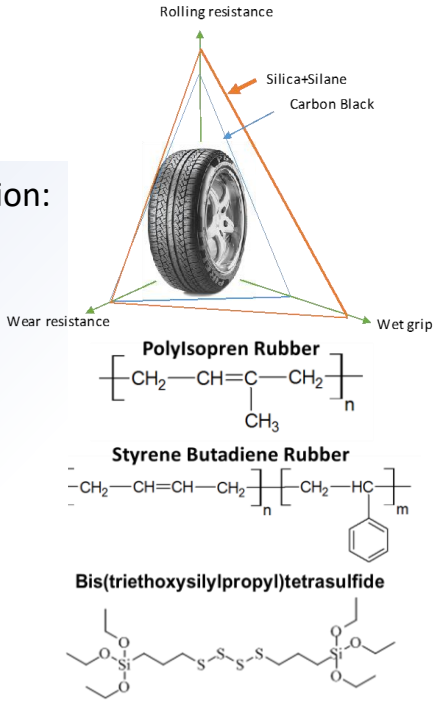




Composite preparation:

First step (crude NC):
Rubber mastication
Silica and compatibilizer addition
Compatibilization

Second step:
Accelerator and Antidegradant
Vulcanization chemicals



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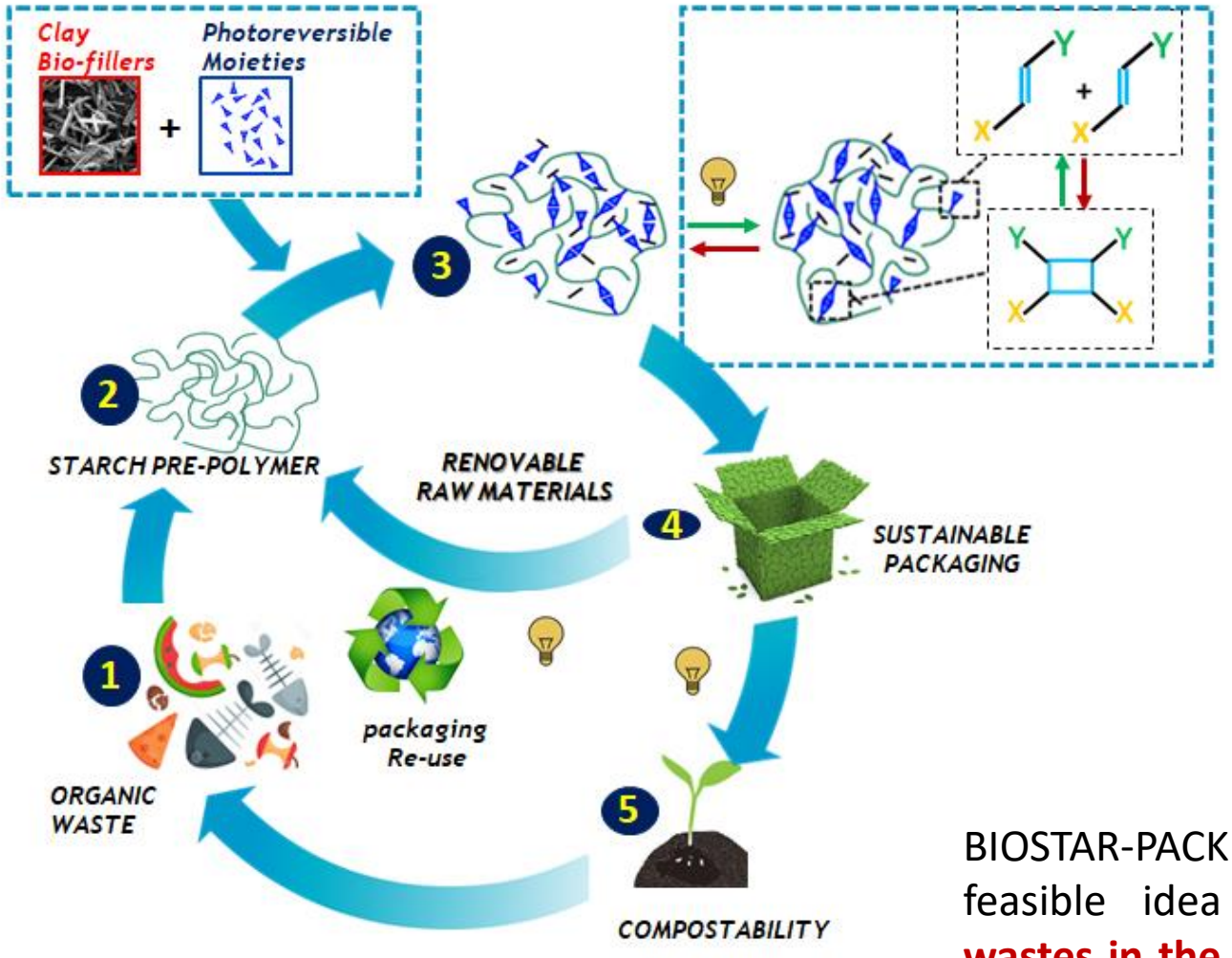
Study the effect on the mechanical behavior of vulcanized rubber compounds due to Fluorsid Silica obtained from Hexafluorosilicic Acid recycling process

Application 5: Recycling & Re-use of oxide materials

On demand BIOdegradable STARrch-derived composites for PACKaging



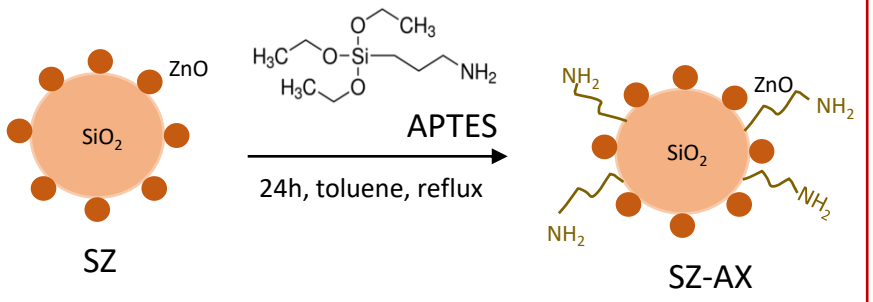
BIOSTAR-PACK proposes an easy and feasible idea to **valorize organic wastes in the development of light-triggered biodegradable composites for food packaging** applications

Fondazione Cariplo 2020-0993, BIOSTAR-PACK (2021-2024)
Massimiliano D'Arienzo- Project coordinator
Università degli studi di Milano-Bicocca (UNIMIB)

Application 6: Photodynamic therapy

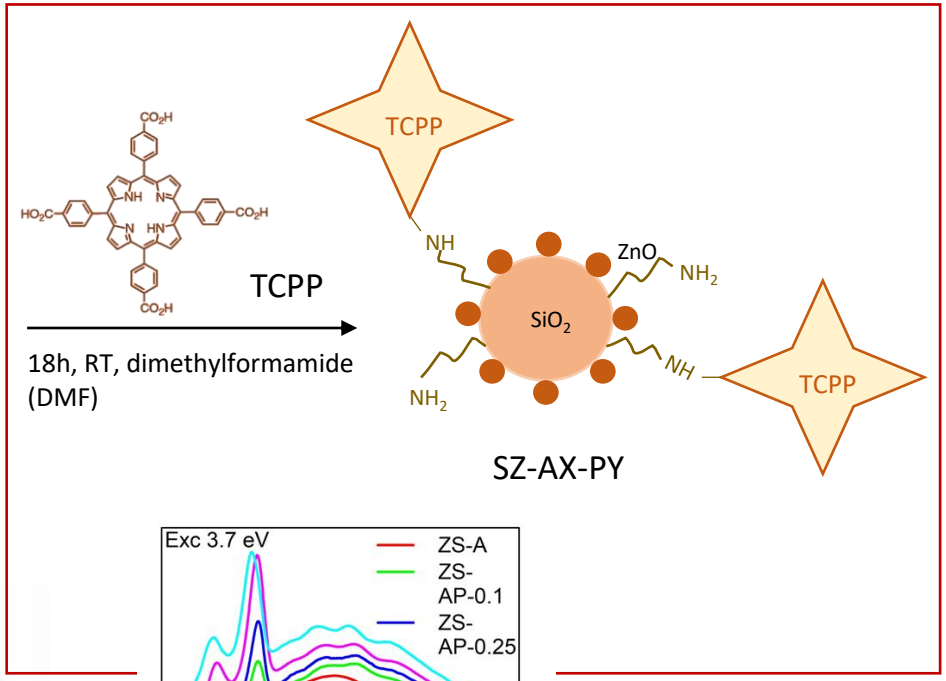
Synthesis of SiO_2/ZnO NPs for photodynamic therapy

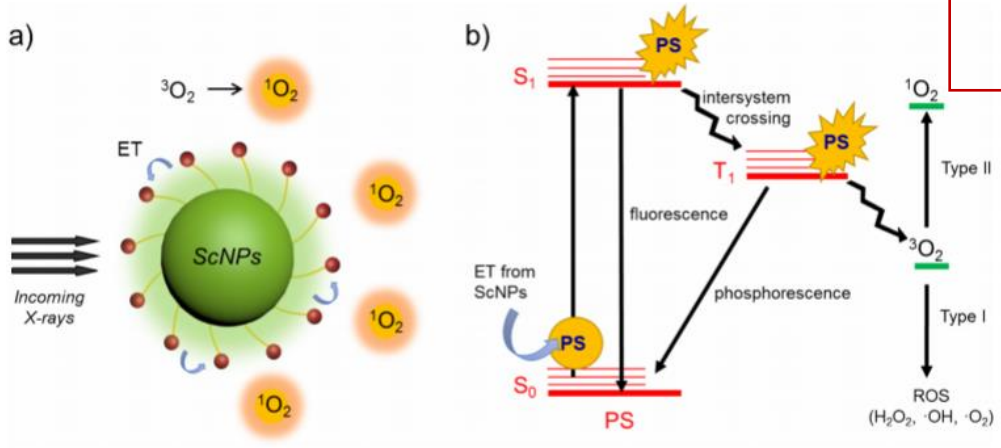
ZnO/SiO_2-porphyrin (TCPP) - different TCPP contents

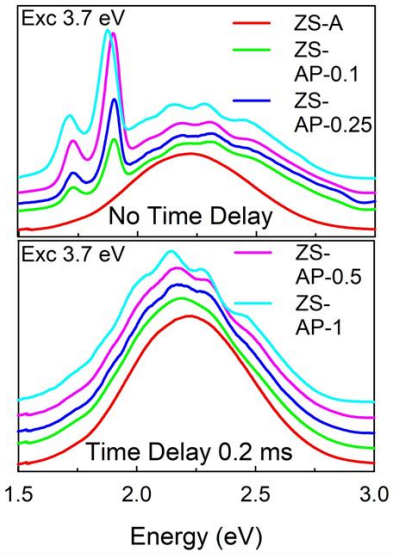


ZS-AX

m_{SZ} = 5.5 g
V toluene = 132 mL
V_{APTES} = 44 µL
wt% APTES/SZ attesa = **0.20%**
X = wt% APTES calcolata da TGA = 0.2%







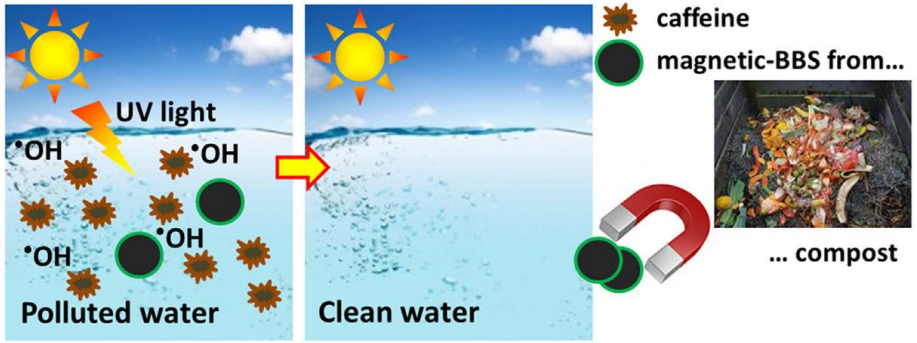
JPCC **2019**, 123, 21651

Nanomaterials **2020**, 10, 1983

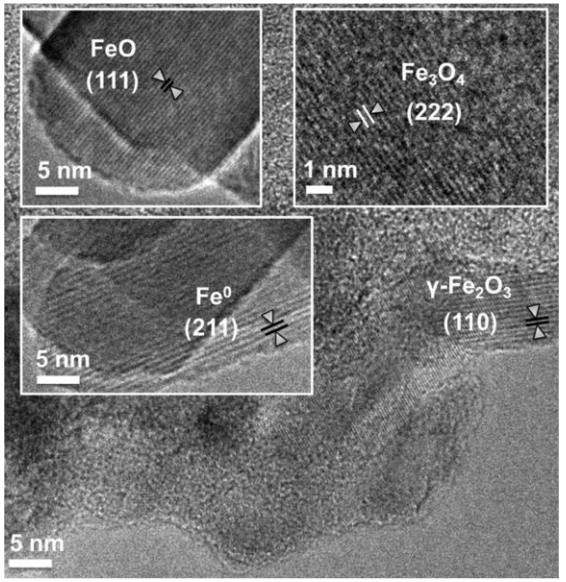
PCCP **2021**, submitted

Application 7:
Magnetic nanomaterials for environmental remediation

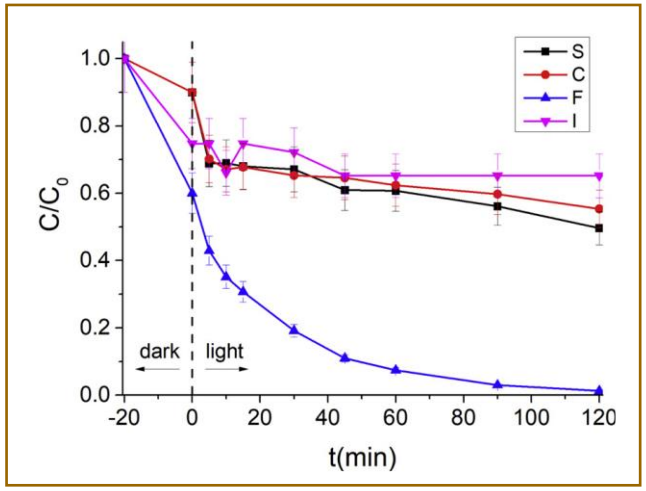
Hybrid magnetic nanomaterials for wastewater treatment



Chem Eng J **2017**, 310, 307

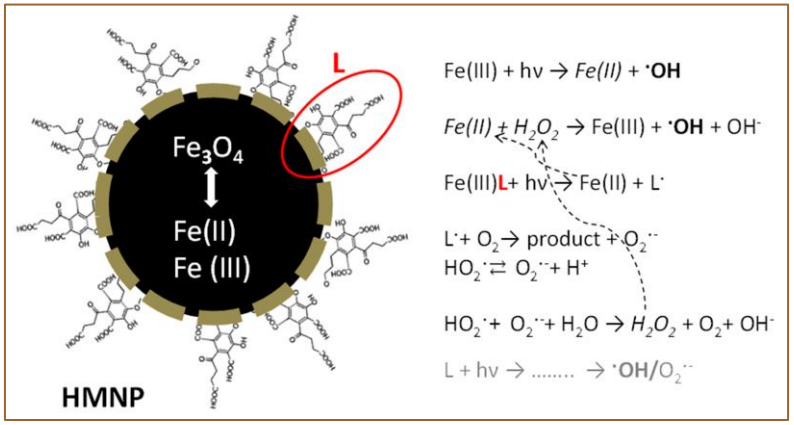


ACS Sustain Chem Eng **2017**, 5, 793



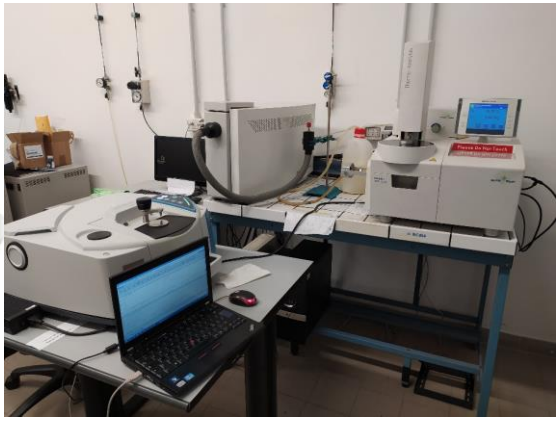
Cat Today **2019**, 328, 164

Photocatalytic abatement of sulfamethoxazole S, carbamazepine C, fluomequine F, and ibuprofen I at circumneutral pH in presence of H_2O_2 (1 mM), and UV radiation.



Materials **2018**, 11, 1084

NanoMat@Lab equipments and facilities



- **Fully equipped labs for preparation of inorganic and composite materials**
- **Characterizations: XRD, TGA, FTIR, DSC, NMR, SEM, TEM**
- **EPR spectroscopy**

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