Active properties of foam coated paper by functionalised nano-fibrillated cellulose

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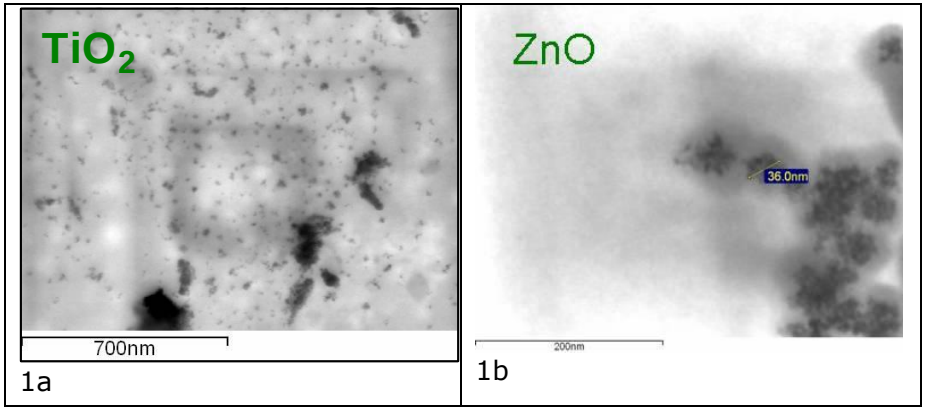
INNOVHUB STAZIONI SPERIMENTALI PER L'INDUSTRIA
SSCCP STAZIONE SPERIMENTALE CARTA, CARTONI E PASTE PER CARTA
Innovazione e ricerca

OBJECTIVE: Production of active paper.

Steps of the work:

- **Functionalisation of NFC by active inorganic nano-particles to produce nano-composites displaying active properties.**
- **Characterisation of nano-composites functionalities.**
- **Deposition of nano-composites on paper and characterisation of paper activity.**

TiO_2 and ZnO inorganic nanoparticles applied for NFC functionalisation.



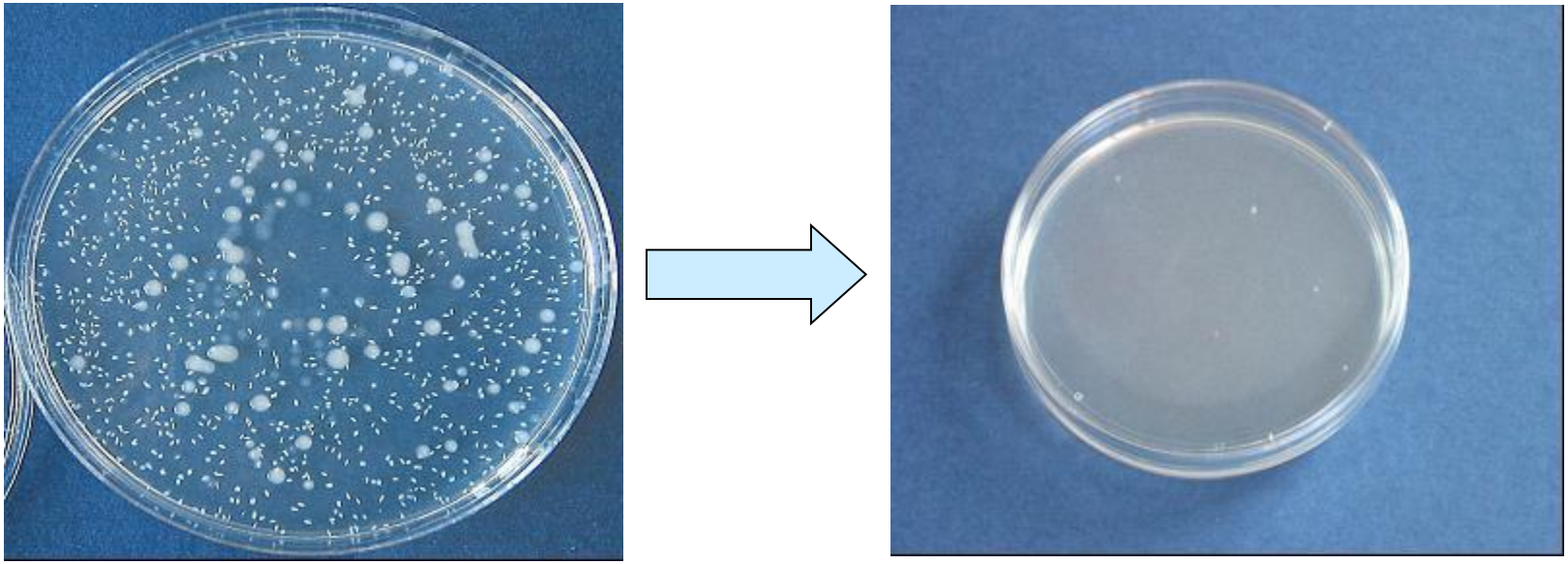
TEM images of TiO_2 and ZnO nanoparticles, dimensions: 40 and 45 nm respectively.

TiO_2 6% water suspension, ZnO 1% diethylene glycol suspension.

Physico-chemical characterisation of inorganic nanoparticles.

		TiO_2	ZnO
Concentration (%w/w)	0.5	6.0	1.0
Density (g/cm^3)	0.05	1.20	1.12
Viscosity (25 C) (mPa.s)	0.1	2.00	ND
Particles Dimension (nm) (DLS Malvern Instruments)		40.0	45.0
Polidispersity Index	0.05	0.25	0.20
pH	0.5	1.0	ND
Cationic surfactant (%w/w)	0.05	0.1	-

TiO_2 and ZnO are known for their active properties: photo-oxidative and antimicrobial activities.



Inhibition to grow (bacteriostatic) or killing (bactericidal) of patogenic bacteria: gram- , gram+ and bacteria spores.

Functionalisation of NFC by the addition of inorganic nanoparticles:

-nano-composites-

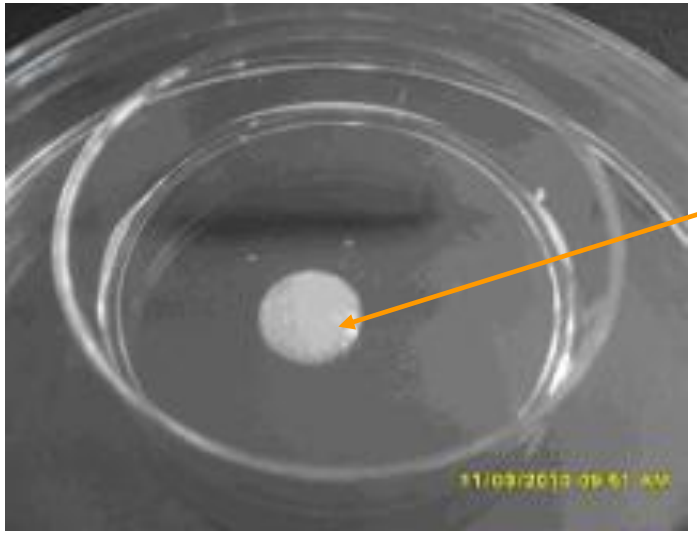
Nano-composites preparation:

- ✓NFC (2.5% in water) + TiO_2 (6% in water) and/or + ZnO (1% in diethylene glicol).
- ✓15 min mixing.
- ✓3 washings with water & centrifugations to eliminate not-adsorbed inorganic fillers.

Nano-composite	Initial mixing ratio of the preparations (as dry weight)	TiO_2 content (% dry weight) (*)	ZnO content (% dry weight) (*)
NFC-TiO_2	1 : 1	24	-
NFC-ZnO	10 : 1	-	7
NFC-ZnO&TiO_2	10 : 1 : 10	42	2

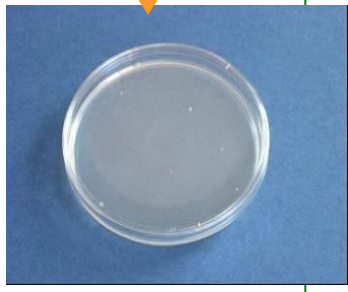
(*) = determined by ICP analysis.

Antibacterial tests on nano-composites.



Nano-composite + bacteria suspension

- ❑ NFC-TiO_2
- ❑ NFC-ZnO
- ❑ NFC-ZnO&TiO_2



Testing conditons.

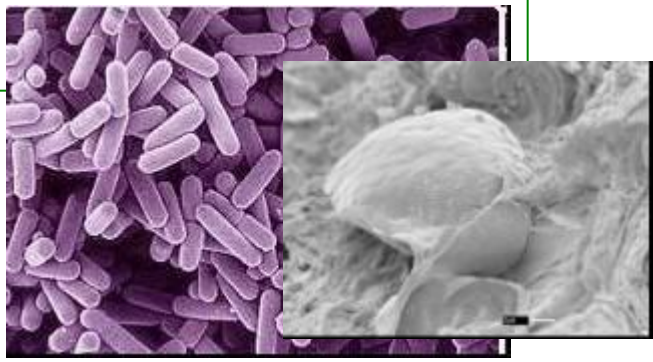
- ➢ Number of living cells initially inoculated: 10^5 (5 log).
- ➢ Exposure: under light (4 hours solar lamp 6.000 lux), or in absence of light (dark conditions).
- ➢ Contact time: 20 hours in optimal bacteria growing conditions (nutrients and Temperature).
- ➢ End of the test: quantitative evaluation of living cells.
- ➢ Bacteria grow on untreated reference (NFC): 10^6-10^7(6 – 7 log).

The nano-composites show antimicrobial activity in conditions of light activation.

	Staphylococcus aureus (gram +)		*Bacillus cereus spores* (gram +)		*Klebsiella pneumoniae* (gram -)	
Sample	**Bacteriostatic activity (log reduction)**	**Bactericidal activity (log reduction)**	**Bacteriostatic activity (log reduction)**	**Bactericidal activity (log reduction)**	**Bacteriostatic activity (log reduction)**	**Bactericidal activity (log reduction)**
NFC-TiO_2	Total bacteriostatic	Complete killing	Total bacteriostatic	1.5	Total bacteriostatic	Complete killing
NFC-ZnO	Total bacteriostatic	Complete killing	Total bacteriostatic	1.4	Total bacteriostatic	4.4
NFC-ZnO&TiO_2	Total bacteriostatic	Complete killing	Total bacteriostatic	1.5	Total bacteriostatic	2.4

Inhibition of bacteria grow: ⟶ **bacteriostatic.**

Killing of bacteria: ⟶ **bactericidal.**



…and also in the absence of light exposition (dark conditions).

	Staphylococcus aureus (gram +)		*Bacillus cereus spores* (gram +)		*Klebsiella pneumoniae* (gram -)	
Samples	**Bacteriostatic activity** (log reduction)	**Bactericidal activity** (log reduction)	**Bacteriostatic activity** (log reduction)	**Bactericidal activity** (log reduction)	**Bacteriostatic activity** (log reduction)	**Bactericidal activity** (log reduction)
NFC-TiO_2	**Total bacteriostatic**	**Complete killing**	**Total bacteriostatic**	**5.0**	**0.5 (low)**	**-**
NFC-ZnO	**Total bacteriostatic**	**Complete killing**	**Total bacteriostatic**	**2.4**	**Total bacteriostatic**	**Complete killing**
NFC-ZnO&TiO_2	**Total bacteriostatic**	**Complete killing**	**Total bacteriostatic**	**2.4**	**1.9**	**-**

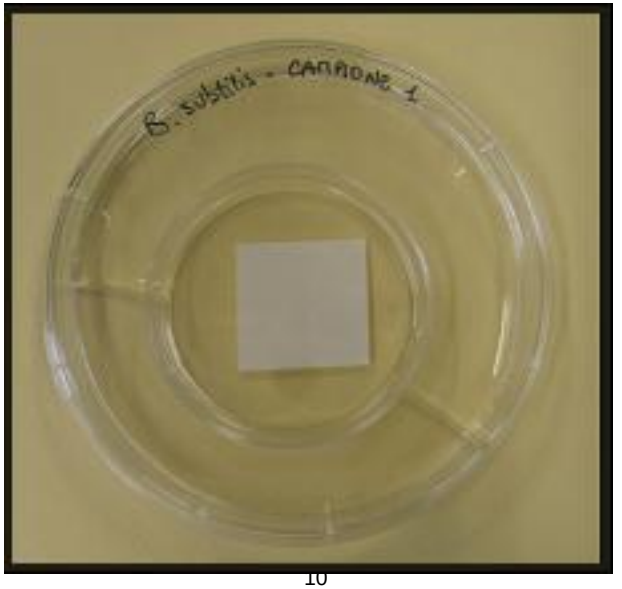
Foam coated papers.

NFC-TiO_2, NFC-ZnO and NFC-ZnO&TiO_2 nano-composites applied on paper: different tested coat weights were tested.

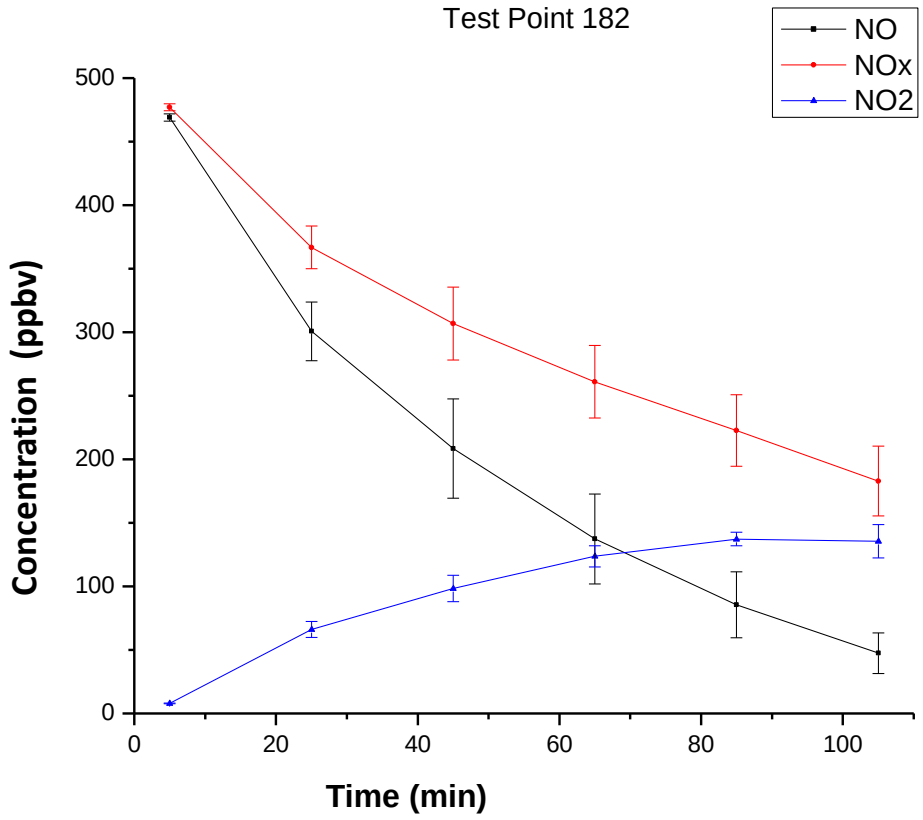
Testing active functionalities of Foam coated papers:

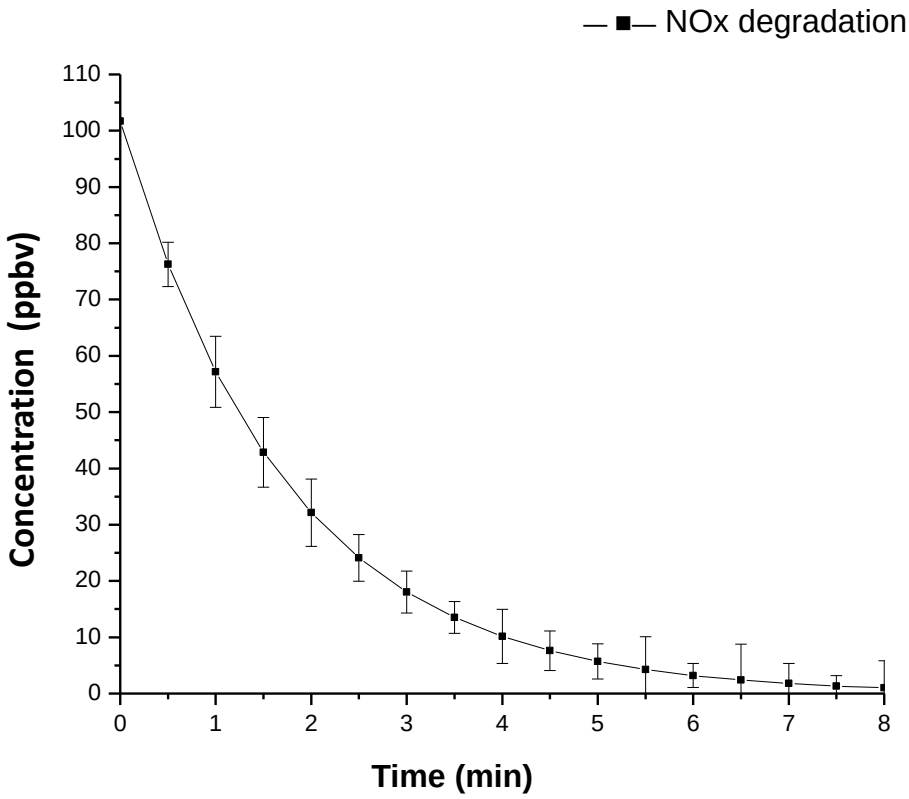
Photodegradation kinetics of NOx in gaseous phase by foam coated papers (photo-reactor equipped with chemiluminescence and GC/MS, Colorobbia).

Antibacterial tests.



Example of Kinetic of NOx photodegradation in gaseous phase by NFC-TiO_2 foam coated paper





NOx photodegradation in gaseous phase by NFC-TiO_2, NFC-ZnO and NFC-ZnO&TiO_2 foam coated papers.

Samples	ppm ZnO (dry weight on paper) ICP analysis	% TiO_2 (dry weight on paper) ICP analysis	% Degradation of NO (after 105 min)	% Degradation of NOx (after 105 min)
Untreated paper (control)	-	-	0	0
Paper NFC-TiO_2 (0.4 g/m^2)	-	0.034	0	0
Paper NFC-TiO_2 (0.9 g/m^2)	-	0.167	72.6	46.0
Paper NFC-TiO_2 (1.8 g/m^2)	-	0.291	79.9	61.6
Paper NFC-ZnO&TiO_2 (0.6 g/m^2)	38.4	0.115	81.7	64.9
Paper NFC-ZnO&TiO_2 (1.3 g/m^2)	104.6	0.307	90.9	78.5
Paper NFC-ZnO (0.8 g/m^2)	180	-	0	0

Antibacterial tests on Foam coated papers under light exposition

Paper Samples	ppm ZnO	% TiO_2	*S.aureus*		*K.pneumoniae*	
			Bacteriostatic activity (log reduction)	Bactericidal activity (log reduction)	Bacteriostatic activity (log reduction)	Bactericidal activity (log reduction)
Untreated paper (control)	-	-	0	0	0	0
Paper NFC-TiO_2 (0.4 g/m^2)	-	0.034	0	0	0	0
Paper NFC-TiO_2 (0.9 g/m^2)	-	0.167	1.3	0	0	0
Paper NFC-TiO_2 (1.8 g/m^2)	-	0.291	Total bacteriostatic	1.0	1.8	0
Paper NFC-ZnO&TiO_2 (0.6 g/m^2)	38.4	0.115	0.7	0	0	0
Paper NFC-ZnO&TiO_2 (1.3 g/m^2)	104.6	0.307	Total bacteriostatic	0.1	0.2	0
Paper NFC-ZnO (0.8 g/m^2)	180	-	Total bacteriostatic	0.3	2.1	0

Antibacterial activity of coated papers *(under dark conditions).*

Paper Samples	% TiO_2	ppm ZnO	*Staphylococcus aureus* (gram +)	
			Bacteriostatic activity (log reduction)	Bactericidal activity (log reduction)
Untreated paper (control)	-	-	0	0
Paper NFC-TiO_2 (1.8 g/m^2)	0.291	-	1.7	0
Paper NFC-ZnO (0.8 g/m^2)	-	180	1.2	0

Conclusions.

- Nano-composites (nanocellulose + inorganic active fillers) display very high antibacterial activity.
- Active nano-composites can be efficiently applied on paper by foam coating, depending on the coat weight active paper can be obtained:
  - antibacterial papers by coating nano-composites containing ZnO and/or TiO_2.
  - active paper for the photo-oxidation of volatile substances in gaseous phase by coating nano-composites containing TiO_2 .

Acknowledgement

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