Addittivi Innovativi a base di nanocellulosa e nanoparticelle inorganiche.

Patrizia Sadocco(*),

Co-authors: Jessica Causio(*), Giovanni Baldi(**), Natercia Martins(***), Carmen Freire(***), Carlos Pascoal Neto(***), Armando Silvestre(***) and Tito Trindade(***)

(*)- Innovhub-SSCCP, (**) Centro Ricerche Colorobbia Italia

(***) CICECO, Departamento de Química, Universidade de Aveiro

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STAZIONE SPERIMENTALE CARTA, CARTONI E PASTE PER CARTA

INNOVHUB
STAZIONI SPERIMENTALI PER L'INDUSTRIA

Innovazione e ricerca

INNOVHUB - Stazioni Sperimentali Industria – Milan, Italy

Azienda speciale della Camera di Commercio di Milano, nata il 1° Ottobre 2011 dalla fusione di 4 diversi Istituti per la ricerca e servizi tecnici per distinti settori industriali: carta, tessili, combustibili, oli e detergenti.

Principale mission: costituzione di un nuovo centro a valenza nazionale per il supporto all'innovazione, sviluppo economico e trasferimento tecnologico per i settori industriali di riferimento.

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SUNPAP

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SUNPAP: Scale Up Nanoparticles in Modern Papermaking

2009-2012

Large scale Integrating Collaborative Project. 7° Framework Programme Theme 4. Nanosciences, Nanotechnologies, Materials and New Production Technologies.

22 different partners from 8 different European countries. Coordinator VTT Finland.

Main objectives of the project:

- Large scale production of nano-cellulose from pulp.
- nanocellulose application in the paper processes to improve the final product performances.
- nanocellulose functionalisation to impart new properties (active, hydrophobic).

The research leading to these results has received funding from the European Community's Seventh Framework Programme under grant agreement nº 228802.

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Obiettivi:

- funzionalizzazione della nanocellulosa (NFC) tramite nanoparticelle inorganiche per la produzione di Nanocompositi con proprietà attive.

- case study: trattamenti superficiali di carta con i nanocompositi attivi.

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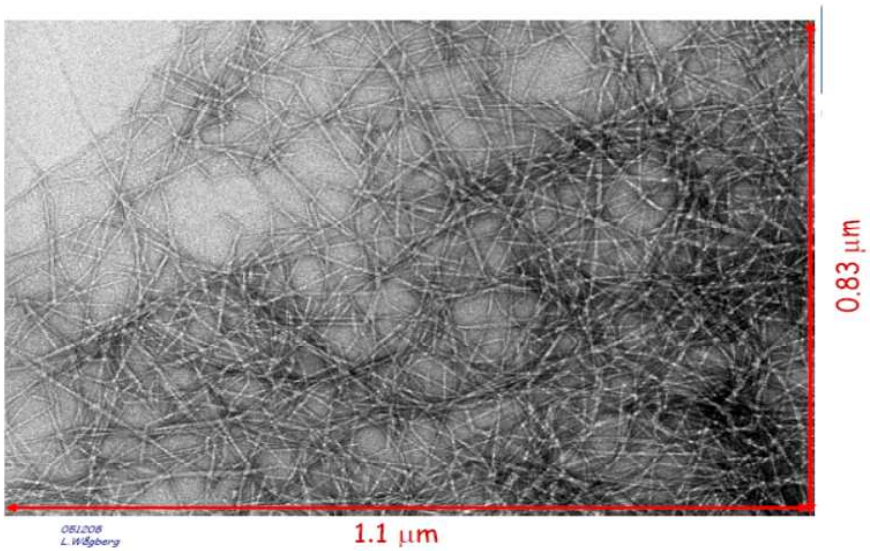
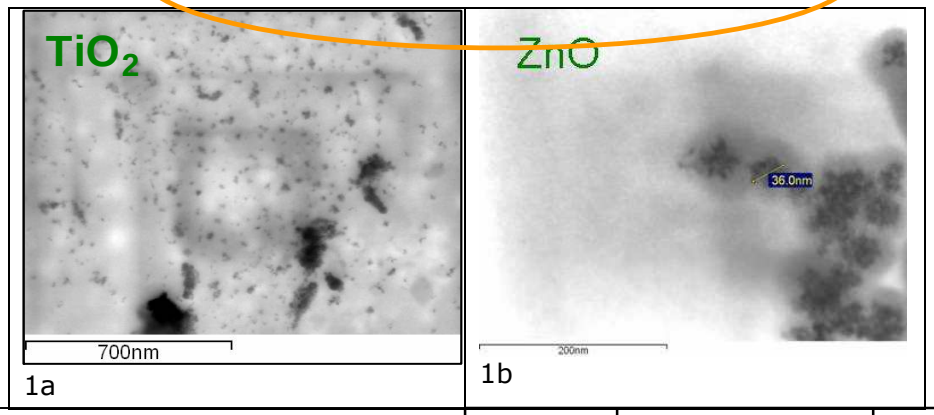
Produzione della nanocellulosa da polpa di cellulosa tramite trattamenti chimici/enzimatici e omogenizzazione. (VTT Finland, CTP France)

Nano-fibrillated Cellulose → gel of cellulose 2% - 4 % consistency.



TEM analysis of nano-cellulose.

Nanoparticelle inorganiche attive utilizzate: TiO_2 e ZnO (Colorobbia, Italy), note per le loro proprietà antimicrobiche.



1a 1b

TEM analysis of TiO_2 and ZnO: 40 and 45 nm diameters, respectively.

	±	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	-

Physico-chemical characterisation:

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

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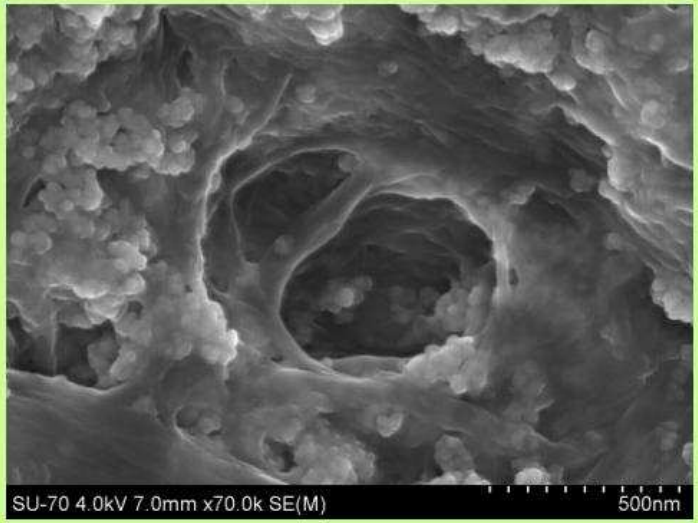


Funzionalizzazione della nano-cellulosa con TiO_2 e ZnO tramite:

a) physical adsorption

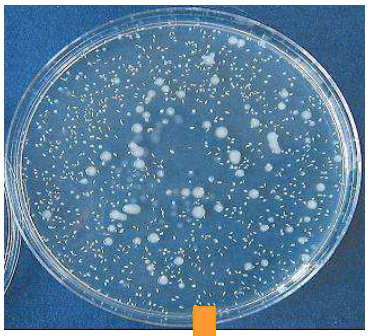
b) deposizione mediata da polielettroliti (electrostatic assembly)

NANOCOMPOSITI

Test antibatterici sui nano-compositi.

Nano-composito + sospensione batterica

- **NFC-TiO_2**
- **NFC-ZnO**
- **NFC-ZnO by electrostatic assembly**



Condizioni di test.

- **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).**

I nanocompositi mostrano attività antibatterica in condizioni di attivazione alla luce.

	Staphylococcus aureus (gram +)		*Bacillus cereus spores* (gram +)		*Klebsiella pneumoniae* (gram -)	
Nano-composite	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 (high)**
NFC-ZnO elettrostatic assembly	**Total bacteriostatic**	**4.5 (high)**	**Total bacteriostatic**	**2.1**	**Total bacteriostatic**	**Complete killing**

Inibizione alla crescita batterica: batteriostatico; uccisione dei batteri inoculati: battericida.

…e anche in assenza di luce.

	Staphylococcus aureus (gram +)		*Bacillus cereus spores* (gram +)		*Klebsiella pneumoniae* (gram -)	
Nano-composite	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**	**1.5**	**0**	**0.3**	**-**
NFC-ZnO	**Total bacteriostatic**	**Complete killing**	**Total bacteriostatic**	**2.4**	**Total bacteriostatic**	**Complete killing**
NFC-ZnO elettrostatic assembly	**Total bacteriostatic**	**4.7**	**Total bacteriostatic**	**3.4**	**Total bacteriostatic**	**Complete killing**

Case studies: applicazione dei nanocompositi per il coating della carta.

Paper size press coating by including active nano-composites in coating formulation (CICECO Aveiro University, Portugal)

A3-size papers sheets, coated with a starch-based coating formulation (6% solid content) containing 20% of nanocomposite with respect to the starch content. Two layers of coating were applied on one side of the paper sheets. Blank samples were also produced using a coating formulation containing only starch. Coating weight on the paper about 3g/mq.

Surface treatment of paper with nano-composites by foam-coating (pilot plant VTT-Finland).

80 g/mq uncalendered fine paper, foam generator: sodium dodecil sulfate. Foam coating parameters: speed machine 100 m/min, air content in the foam 90%, pumping rate 30 l/h. Final coating weight around 1 g/mq.

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Proprietà attive di carte trattate con nanocompositi

<u>Fotodegradazione di composti volatili.</u> Analysis of the oxidation of NOx in gaseous phase by a photoreactor equipped by chemiluminescence and GC/MS analysis (Colorobbia)

<u>Attività antibatterica.</u>

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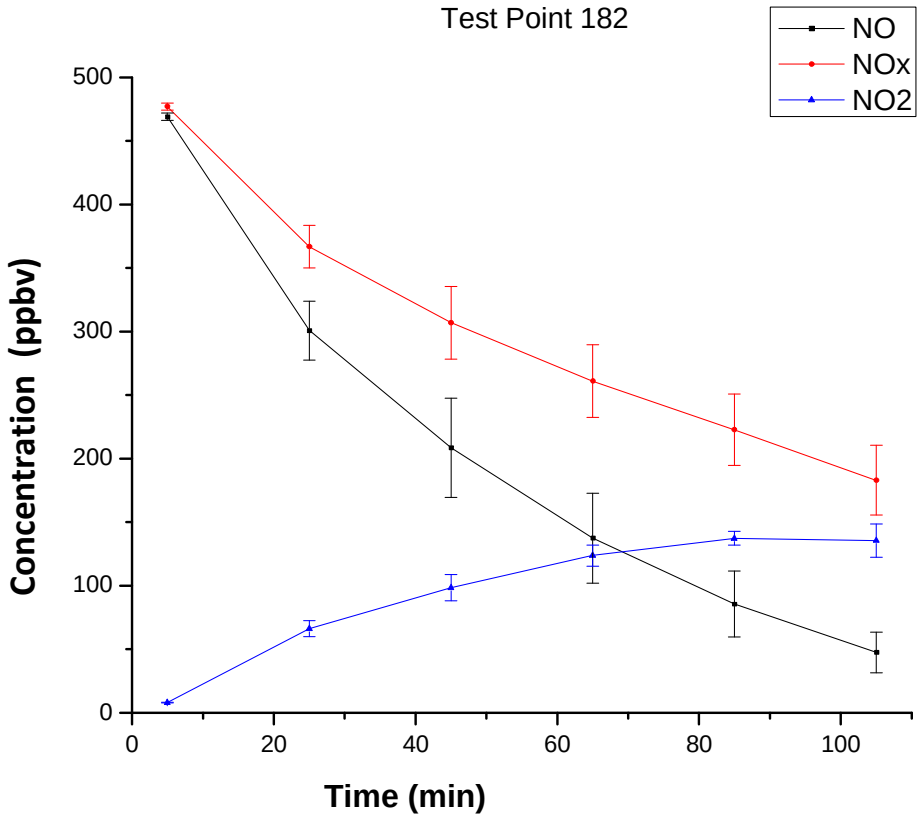
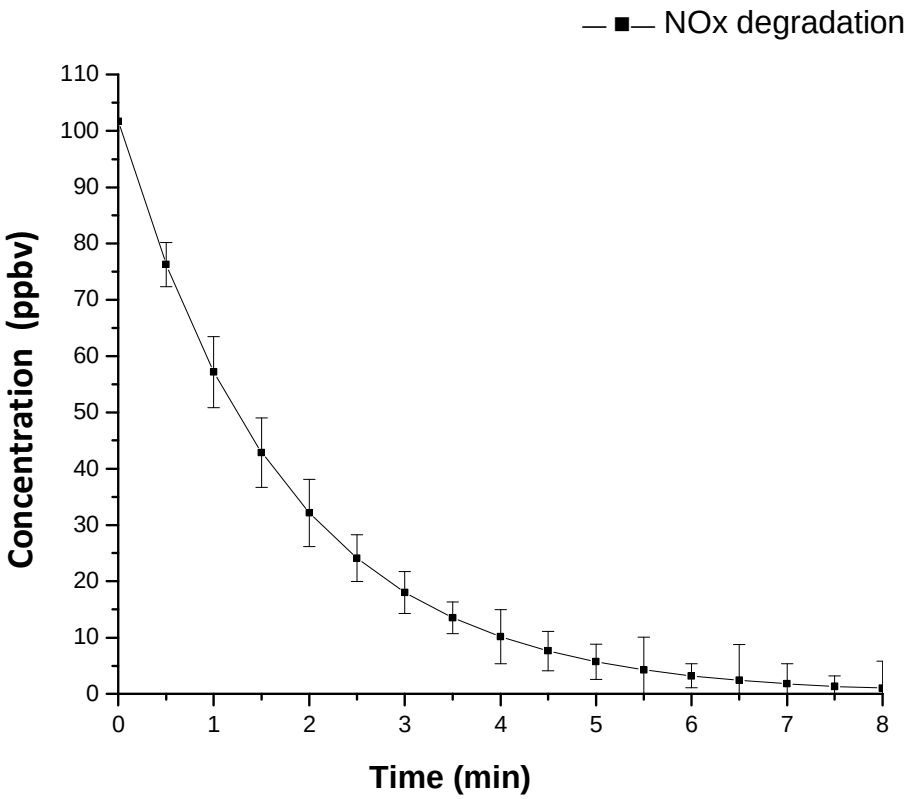
Example of Kinetic of NOx photodegradation in gaseous phase by NFC-TiO_2 foam coated paper





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Fotodegradazione di NOx in fase gassosa: papers treated by nano-composites (foam-coated and size press coating).

Paper Samples	% TiO_2 (dry weight on paper) ICP analysis	ppm ZnO (dry weight on paper) ICP analysis	% Degradation of NO after 105 min	% Degradation of NOx after 105 min
Untreated paper (control)	-	-	0	0
Carta trattata tramite foam coating con NFC-TiO_2	0.291	-	79.9	61.6
Carta trattata tramite foam coating con NFC-ZnO	-	180	0	0
Carta trattata Starch Size press con NFC-ZnO	-	136.5	0	0

Attività antibatterica di carte trattate *(under light activation).*

			Staphylococcus aureus (gram +)		*Klebsiella pneumoniae* (gram -)	
Paper Samples	% TiO_2	ppm ZnO	Bacteriostatic activity (log reduction)	Bactericidal activity (log reduction)	Bacteriostatic activity (log reduction)	Bactericidal activity (log reduction)
Untreated paper (control)	**-**	**-**	**0**	**0**	**0**	**0**
Carta trattata tramite foam coating con NFC-TiO_2	**-**	**180**	**Total bacteriostatic**	**1.0**	**2.1**	**0**
Carta trattata tramite foam coating con NFC-ZnO	**-**	**136.5**	**Total bacteriostatic**	**1.4**	**Total bacteriostatic**	**1.7**
Carta trattata Starch Size press con NFC-ZnO (electrostatic assembly)	**-**	**228**	**Total bacteriostatic**	**1.6**	**Total bacteriostatic**	**1.1**

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
Carta trattata tramite foam coating con NFC-TiO_2	0.291	-	1.7	0
Carta trattata tramite foam coating con NFC-ZnO	-	180	1.2	0
Carta trattata Starch Size press con NFC-ZnO	-	136.5	Total bacteriostatic	2.2

- Conclusioni-

Applicazione di nano-compositi nelle formulazioni per il coating della carta può essere un interessante approccio per produrre carte con proprietà attive:

- proprietà antimicrobiche

- degradazione di composti volatili inorganici.

- degradazione di composti volatili organici (ad es. etilene) di interesse per il food packaging: *work in progress*.

Grazie dell'attenzione!

patrizia.sadocco@mi.camcom.it

sunpap.vtt.fi

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