Nano-sized materials in antimicrobial protective clothing

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- General aspects of antimicrobial in textiles
- Nano-sized materials as antimicrobial agents in textiles
- Future challenges and perspectives

Antibacterial textiles

- Textiles, having large surface area and being capable to retain moisture favor microorganism growth, in particular in humid environment
  - Development of unpleasant odor
  - Fabric deterioration (additives, colorants, elasticity etc.)
  - Contamination risks

- Applications of antibacterial textiles include healthcare, hygiene, sportswear, automotive textiles, ventilation and air conditioning, water purification etc.

Antimicrobial treatment of textile

- Incooperation during fiber spinning process
- Treatment in the finishing state

- Efficiency against microorganisms
- Durability to cleaning processes (laundry, dry cleaning, hot pressing etc.)
- No effect on textile performance & hand
- User' safety (cytotoxicity, allergy, irritation and sensitization)
- Safe handling & environmental friendliness

Antimicrobial mechanisms and types

- Biostatic: inhibition of cell growth, preventing the multiplication of bacteria
- Biocidal: killing the microorganisms, causing the rupture of the cell outer layer and membrane and damage the cell

- Leaching type: moving from the surface and entering the microorganisms
- Bound type: making the surface antimicrobial active and rupturing the cell membrane by direct contact

Antimicrobial agents in textiles

- Quaternary ammonium compounds
- Triclosan
- Metals / metal oxides and metallic salts
- Chitosan
- Regenerable N-halamines
- Poly(hexamethylene biguanide)
- Natural-based antimicrobial agents

Nano-sized antimicrobial agents

Particle	Mechanism	Example on antimicrobial effect MIC
Ag	Disruption of cell membranes Interference with DAN replication	*Escherichia coli, Vibrio cholerae* almost 100% at 73µm/mL (21nm)
Cu	Inactivation of protein	*Escherichia coli, Bacillus subtilis* by 90% at 33 µm/mL (100nm)
ZnO	Disruption of cell membranes, reactive oxygen inhabitation	*Staphylococcus aureus and Escherichia coli* by 99% at 400 µg/mL (40nm)
Fe_3O_4	Disruption of cell membranes, reactive oxygen inhabitation	*Staphylococcus aureus* by 65% at 2mg/mL (8nm)

Silver as antibacterial agent

- Membrane disruption / Interference with DNA replication / Generation of reactive oxygen species (ROS)
- Higher antibacterial activity due to the high surface-to-volume ratio, providing better contact with microorganisms
- Example: Ag nanoparticles (~ 21 nm) inhibit (almost completely) the growth bacteria species *Escherichia coli, Vibrio cholerae, Salmonella typhi*, and *Pseudomonas aeruginosa* on agar plates with nanoparticle concentrations at or above 75 μg/mL.

Copper as antibacterial agent

- Protein inactivation via thiol interaction.
- Copper nanoparticles (~ 100 nm) reduce *Escherichia coli* and *Bacillus subtilis* survival by 90% at concentration of ~ 30 µg/mL. The growth of both bacteria species was completely inhibited at nanoparticle concentrations above 60 µg/mL.
- Activity even higher compared to Ag nanoparticles with ~40 nm diameter (in some comparative studies)

Zinc oxide as antibacterial agent

- The production of hydrogen peroxide seems to attribute to bactericidal activity
- Zinc ions are known to inhibit multiple activities in the bacterial cell, however, likely only contribute inhibit bacteria proliferation
- Example: ZnO (~40 nm) inhibites the growth of *Staphylococcus aureus* and *Escherichia coli* by 99% at 400 μg/mL.

Iron oxide as antibacterial agent

- Not common, but some studies showed the effect of Fe_3O_4 on the inhibition of bacteria activity, based on the ability of nanoparticles to penetrate into the cell and generate reactive oxygen species.
- Relatively high concentrations of nanoparticles, however, are needed
- Example: Fe_3O_4 (~9 nm) in chain-like structure with a length of 100–200 nm to reduce *Staphylococcus aureus* viability at 3 mg/mL

Interaction between clothing and microbes

is a function of the ability of microbes to adhere onto fiber surfaces (i.e. biofilm formation), fiber hydrophilicity, levels of unbound surface water, and polymer susceptibility to hydrolysis by microbial enzymes:

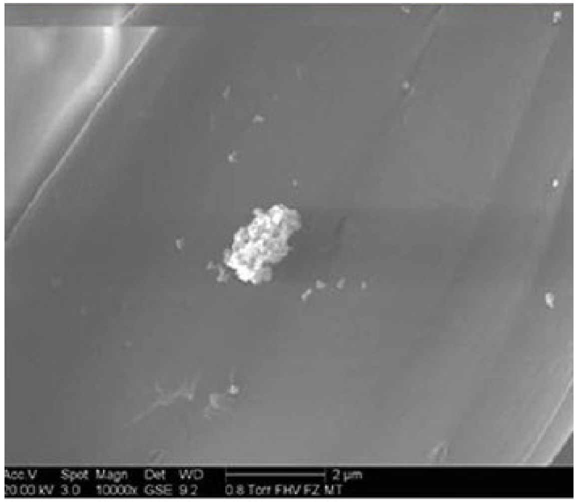
- Natural fibers and regenerated cellulosics (e.g. cotton, wool and viscose rayon) are hydrophilic, exhibit rough surfaces that promote microbial adhesion, and the polymer structures are susceptible to hydrolysis by microbial enzymes.
- Animal hair fibers are found more susceptible to bacteria, while cellulosics more to fungi
- Synthetic fibers (e.g. polyester, nylon) are hydrophobic, exhibit smooth surfaces that hinder microbial adhesion, and their polymer structures are not susceptible to enzymatic hydrolysis – and therefore are not prone to microbial degradation.

AgNPs incooperarion in clothing

- Impregnating substrates with colloidal Ag solutions of pre-formed NPs (dispersions of silver metal particles)
- Impregnating substrates with solutions of Ag salt and further treating with reducing agents to convert into AgNPs
- However, the key issue with topical application of Ag particles on clothing remains their durability
- Concerns of AgNPs on their potential for causing harm either to humans or the environment, e.g. risk of inhalation and impact on flora and fauna etc.

Formation of Ag from $AgNO_3$ in textiles

cellulose fibers in 0.941 mmol/l $AgNO_3$



Sample[a]	Reduction in bacteria			
	1 min	10 min	30 min	60 min
a. Untreated	0%	0%	0%	0%
b. 1.62 ± 0.68 μmol Ag/g Fiber	30%	100%	100%	100%
c. 6.40 ± 1.56 μmol Ag/g Fiber	84%	100%	100%	100%

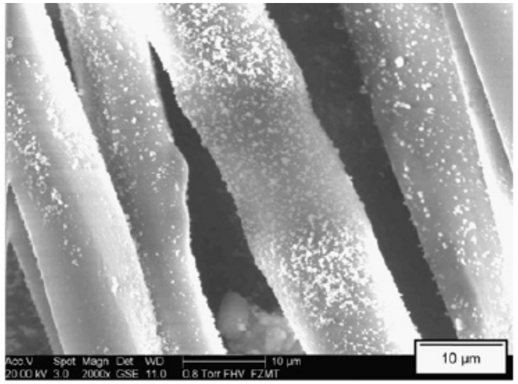
[a] CLY fibers treated with $AgNO_3$ solutions at 30 °C.

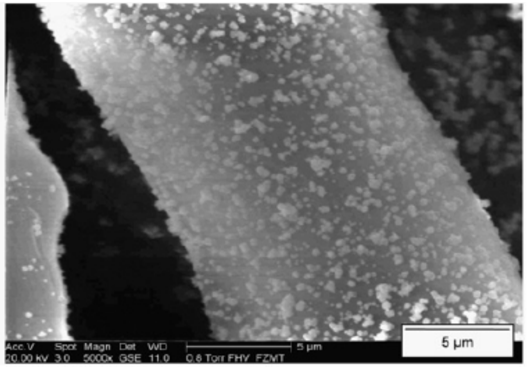
Wash cycles	CLY	
	Ag content (μmol/g)	Loss (%)
Unwashed	5.11 ± 0.58	–
1	2.98 ± 0.40	41.75
5	1.04 ± 0.14	79.56

- Ag particles in the size range of ca. 25 - 300 nm
- Antimicrobal activities at levels similar to those reported in literature for AgNP containing substrates.
- Significant inherent adherence of particles on fibers, which may be further improved with fixation treatments commonly employed in textile processing.

H.E. Emam et al. / Journal of Cleaner Production 39 (2013) 17–23

Copper oxide surface modified cellulose fibers





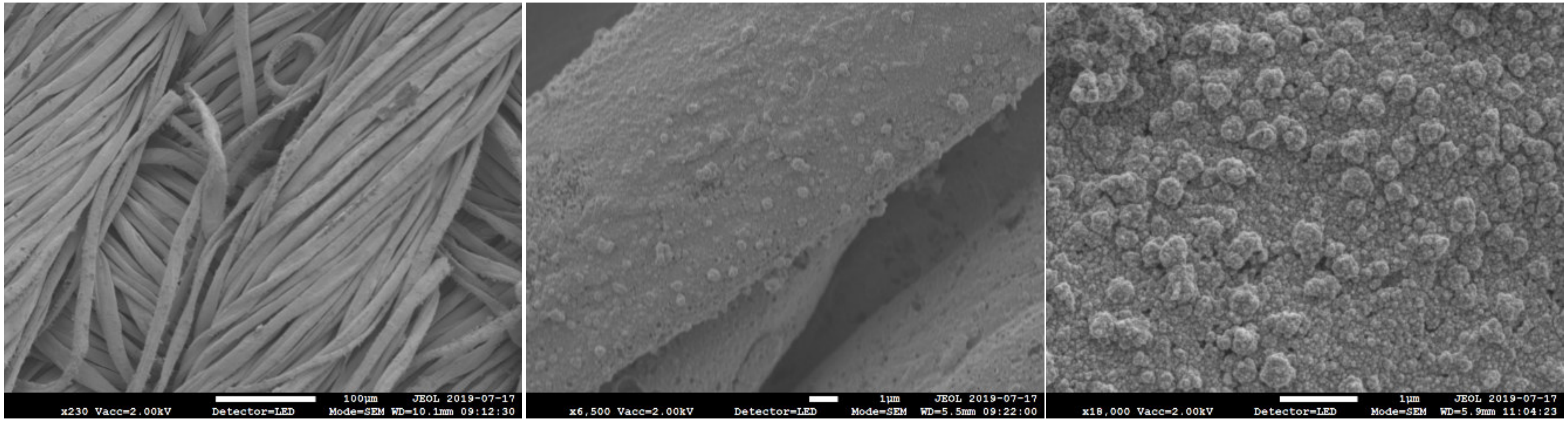
- Formation of Cu_2O ligand exchange reaction using solutions of Cu–DGL complexes
- Slow reduction of Cu^{2+} by DGL, which crystallizes on the fiber.

Fabric samples	Cu content (mmol/kg)	Bacterial reduction/%			
		1 min	1 h	3 h	6 h
Blank	0	0	0	0	0
pH 10	18.49	6.9	80.2	99.9	100
pH 10/5× wash	3.53	0	45.7	99.2	100
pH 10/$NaBH_4$	17.61	12.3	99.8	100	100
pH 10/$NaBH_4$/5× wash	2.62	0	99.5	100	100
pH 13	23.7	16.9	98.6	99.7	100
pH 13/5× wash	3.26	0	61.9	91.4	100
pH 13/$NaBH_4$	19.47	0	61.9	100	100
pH 13/$NaBH_4$/5× wash	6.16	0	99.3	100	100

Wash-cycles	Cu–DGL			
	pH 10/0.5 M		pH 13/0.1 M	
	mmol/kg	Loss %	mmol/kg	Loss %
–	18.5 ± 0.8	–	23.7 ± 4.3	–
1	13.0 ± 2.4	29.5	17.5 ± 2.9	26.0
5	3.5 ± 0.8	80.9	3.3 ± 0.6	86.3

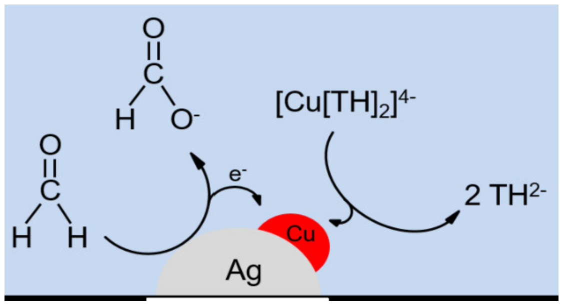
H.E. Emam et al. / Surface & Coatings Technology 254 (2014) 344–351

Deposition of Cu on Ag seeds



Metal deposition on Ag seeds

$$Cu^{2+} + 2H_2CO + 4OH^- \rightarrow Cu^0 + 2HCOO^- + 2H_2O + H_2$$



- Primary / secondary Cu particles clusters, depending on process parameters
- Flexible structure combined with high conductivity

J. Landsiedel et al, GÖCH Meeting 2019
W. Root et al, Surface & Coatings Technology 348 (2018) 13–21

Future challenges and perspectives

- Regulations on nano materials, including Biocidal Products Regulation (BPR) and nanomaterials – Risk assessment !
- Application environments ?
- When is „nano“ really needed ?
- Bulk vs. surface modification ?
- Phase bounding between NPs and textile substrate vs. durability vs. antibacterial effectiveness > interface chemistry !
- “Rechargeable” antibacterial reservoirs ?
- Technological concepts for economical generation of antibacterial materials and incooperation into/onto textiles
- Nanoparticles in environmental cycles