Review

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Metal nanoantimicrobials for textile applications

Abstract: Research on the nanomaterials containing one or more transition metals is growing tremendously, thanks to the large number of preparation processes available and to the novel applications that can be envisaged in several fields. This review presents an overview of the selected studies in the field of antimicrobial textiles, employing bioactive nanophases of elements/compounds such as silver, copper, or zinc oxide. In addition, the history of use of these antimicrobials and their mechanism of action are shortly reported. Finally, a short description is provided of the deposition/preparation methods, which are being used in the authors' labs for the development of the textiles modified by the novel nanoantimicrobials.

Keywords: copper; nanoantimicrobial; textile; silver; zinc oxide.

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1 Introduction

In the last decades, several research and industrial efforts have been devoted to the development of new products for enhancing the quality of human life. The textile production, one of the most relevant and ever-advancing industrial field around the world, is not an exception. In particular, with a rising awareness in personal health and hygiene, the textiles with antimicrobial properties are becoming an appealing field for both the manufacturers and researchers [1–26].

The antimicrobial agents are generally used to avoid three undesirable effects in textiles [10]. The first is regarding the characteristic degradation phenomena of fabrics, like coloring, staining, and deterioration of the fibers [27–29]. The second one is the production of unpleasant odor [30–32], and the last one is the increase of potential health risks [1, 33–36]. Besides, the polymeric and especially natural fibers have no resistance against microorganisms and their metabolites, as well as they are most commonly responsive to accumulation, multiplication, and proliferation of the microorganisms [30–32, 34, 37, 38]. When in contact with the human body, the textiles offer an ideal environment for microbial growth because of their large surface area, ability to retain oxygen, moisture and warmth, suitable temperature and humidity, as well as nutrients from spillages and body exudates [39]. Therefore, various antibacterial finishing and disinfection techniques are being developed for all the types of textiles: from hospital environment (medical clothes, protective garments, wound bandages, etc.) to everyday household and clothing.

In general, the antimicrobial properties can be imparted to the textile materials by chemically or physically incorporated functional agents onto the fibers or fabrics. Almost every class of chemical compound has been tested to confer the antibacterial activity to the textiles. The chemical agents in use for controlling the microorganisms ranged from the very simple substances such as halogen ions to very complex compounds [40–42]. In the last decades, using many antimicrobial agents without a tight control over their bioactivity has been stopped because of their possible undesired harmful or toxic effects [10].

Differently from some organic compounds, which have also been employed in the textile finishing processes such as the antibacterial agents, the metal nanoparticles

(NPs) represent a good alternative, providing new bioactivity mechanisms and allowing the multifunctional modification of the textiles. The nanomaterials range from the nanometals, such as silver and copper NPs, to the metal oxides, such as titanium or zinc oxides [43], to the carbon nanotubes (CNT) and clays.

The current textile products have been progressed so much that many of them are designed to inhibit the microorganisms' growth and proliferation, thus, contributing to prevent the disease transmission; moreover, these modifications are tailored to be effective for a long-term period. The cutting edge in this field is the development of efficient, nontoxic, durable, and cost-effective antimicrobial finishing textiles with increased applications in medicine, health care, and in the development of hygienic products as well as protective textile materials [43–45].

The antimicrobial textiles exclusively employing drugs or other organic/molecular biocides are not reviewed in this paper, which is, on the contrary, focused on the current research on innovative textile fibers modified with metal nanoantimicrobials. These novel products possess good antimicrobial properties due to the presence of the bioactive metals such as silver, copper, and zinc in the forms of nanophases containing ions, oxides, or complexes. The extensive citation of the studies related to the bioactivity mechanisms involving the aforementioned ions and metals is provided as well. This also because ionic release is at the basis of the important bioactivity mechanisms of the mentioned nanoantimicrobials. Finally, a brief mention of the novel textile modification methods developed in the authors' laboratories is provided.

2 History and antimicrobial mechanisms of silver, copper, and zinc oxide

Some bioactive elements and oxides, such as Ag, Cu, and ZnO, either as such or when they are dissolved in the form of ions or complexes, possess wide-spectra antimicrobial properties. Indeed, these antimicrobial properties are known since ancient times. Therefore, a short description of the uses of these elements as antimicrobial agents is presented in the next paragraphs to understand why silver, copper, and zinc have become the interesting agents for disinfecting the textiles. The ability of an organism to accumulate antimicrobial metal species from the environment is critical for its growth and survival. The mechanisms of action of these elements (as well as the resulting nanophases) have not been understood completely; however, some information about the metal-microorganism interactions are reported in the following subsections.

2.1 Silver: history and mechanisms of action

Silver and its antimicrobial properties are known since antiquity. For thousands of years, silver has been used as a healing and antibacterial agent by the civilizations throughout the world. Its medical, preservative, and restorative powers can be traced back to the ancient Greek and Roman Empires. Before the development of modern pharmaceuticals, silver was employed as a germicide and antibiotic. The Greeks used silver for water purification, and Pliny the Elder, the famous Roman physician, reported on the properties of silver in his encyclopedia (79 AD) [46]. The use of silver is mentioned in the ancient Egyptian writings. Hippocrates, the father of modern medicine, believed silver powders to have a beneficial healing for ulcer [47]. Since the 19th century, many studies were carried out, and many applications of silver were employed in the different fields of medical research [48]. In Germany (1884), Carl Siegmund Franz Credé introduced an eye prophylaxis to prevent ocular infection by using silver nitrate solution on neonates [49]. In the 1920s, colloidal silver was accepted by the US Food and Drug Administration (FDA) as being effective for wound management [50], and through the first half of the 20th century, it was used to control infections in burn wounds [49].

A variety of mechanisms may be involved in the antimicrobial activity of silver toward several microorganisms. Some of the commonly accepted mechanisms include the silver-amino acid interaction, silver-DNA interaction, generation of reactive oxidative species (ROS), and direct cell membrane damages [10, 29, 51–65].

First of all, the interaction between the metal ions and thiol groups in the proteins or enzymes of the microorganisms leads to the inhibition of most of their biological functions [66–70].

Feng et al. [71] have reported the antibacterial mechanism of Ag^+ on *Escherichia coli* and *Staphylococcus aureus* bacteria showing that after silver treatment, electron dense granules were generated by cell self-defense mechanism to protect the DNA. This has been confirmed in another work by Yang et al. [72].

Silver ions can also generate an excess of ROS which are extremely deleterious to the cells, causing damages to the lipids or DNA. It has been shown that *E. coli* have two proteins as ROS-sensing systems: SoxR and

OxyR [73]. When exposed to the superoxide or nitric oxide radicals, SoxR protein induces a single-gene *soxS*, and by monitoring the soxS induction in the reporter strains, the ROS level in the solution can be determined. Therefore, the generation of the ROS is a plausible biocidal pathway and also suggests that the antibacterial mechanisms of silver ions are a combination of ROS generation and silver-thiol interactions [73].

Bard and coworkers [74] have reported the inhibition of respiration of *E. coli* cells treated by silver ions. The mechanism of action involves silver ions that are able to make the cell membrane permeable to protons; therefore, to compensate the loss of proton gradient, the acceleration of respiratory process is triggered, attempting to expel more protons to restore the proton gradient. This uncontrolled process generates the superoxide or hydroxyl radicals, which are extremely harmful to the cells.

Finally, the direct damage to the cell membranes caused by the silver nanomaterials has been reported recently by Morones et al. [75]. The detailed mechanism of the cell membrane penetration and accumulation of the silver NPs is not fully understood. One hypothesis is that the accumulation is caused by the electrostatic attraction between the negatively charged bacterial surfaces and positively charged silver NPs [76]. However, this does not explain why the negatively charged silver NPs are able to adhere and enter the bacterial cells. Another possibility is that the process is initiated by silver-thiol group interaction on the cell surface, as it is hypothesized in a recent publication [77].

A further explanation for the cell membrane damage is proposed for the Gram-negative bacteria such as *E. coli*. The Gram-negative bacteria possess an external membrane outside the peptidoglycan layer, which is lacking in Gram-positive bacteria. It was previously found that the chelating agent EDTA can cause the depletion of Ca^{2+} and Mg^{2+} ions, resulting in pits and holes in the outer membranes due to the release of the lipopolysaccharide (LPS) molecules [78]. Sondi et al. [79] also observed a similar phenomenon by treating *E. coli* bacteria with silver NPs. They showed SEM images clearly highlighting the presence of many holes in the cell membranes of the silver-treated *E. coli*. It was also hypothesized that silver may generate pits and holes in the cell membrane by the aforementioned LPS-release mechanism [79].

2.2 Copper: history and mechanisms of action

The disinfecting power of copper was discovered by the ancient Greeks. They had easy access to copper as this metal was readily available on the island of Kypros (Cyprus) from which the Latin name for copper, cuprum, is derived. They purified drinking water with copper and prescribed it for diseases affecting the lungs. Copper was used by the ancient Egyptians in order to sterilize wounds and drinking water. During the reign of Tiberius (14 to 37 AD), copper and its derivatives had been firmly established as an important drug in the medical practitioner's pharmacopoeia. The Aztecs also used copper for medical purposes, while in Persia and India, copper was applied to treat numerous infections [80, 81]. The Celts produced whisky in copper vessels in Scotland, and copper strips were nailed to the ship's hulls by the early Phoenicians to inhibit fouling. In the western world (18th century), copper was employed for the treatment of mental disorders and pulmonary diseases. In the 19th century, the first observation of the copper's role in the immune system was published in 1867 when it was reported that, during the cholera epidemics in Paris, copper workers were immune to the disease. The early American pioneers put silver and copper coins in large wooden water casks to disinfect the drinking water like the Japanese soldiers that, during the World War II, used to place pieces of copper in their water bottles to prevent dysentery. One of the first surveys on the historic use of copper medicinal substances was proposed by J. R. J. Sorenson [82]. The same author demonstrated that the copper complexes have a therapeutic efficacy in the treatment of inflammatory diseases using doses that are nontoxic [83, 84]. Copper sulfate is highly prized by some inhabitants of Africa and Asia for therapeutic sores and skin diseases. Finally, NASA first designed an ionization copper-silver sterilizing system for its Apollo flights [82, 85].

Nowadays, copper is used as a water purifier and as an antibacterial and antifouling agent [33]. Introducing copper into clothing, bedding, and other articles would provide them with biocidal properties [86]. However, copper is also an essential element required by all the living organisms as it is an important cofactor for a variety of enzymes that are required for the essential biochemical processes such as cytochrome c oxidase, Cu-Zn superoxide dismutase, lysil oxidase, and dopamine-ß-hydroxylase [87].

Several mechanisms for the biocidal activity of copper have been proposed. These include the production of hydroxyl radicals, which cause cellular damage such as the oxidation of proteins, cleavage of DNA and RNA molecules, and membrane damage due to lipid peroxidation [85].

The copper's initial site of action is thought to be at the plasma membrane [85, 88–90]. It has been shown

that the exposure of fungi and yeast to the extremely high copper concentrations can lead to a rapid decline in membrane integrity. This generally manifests itself as leakage of mobile cellular solutes, such as potassium ions, and cell death. Similar effects reported in higher organisms have now been largely attributed to the redox-active nature of copper and its ability to catalyze the generation of the free radicals that promote membrane lipid peroxidation [91–93].

After the completion of its genome sequence, *Saccharomyces cerevisiae* yeast has become a model organism for elucidating the mechanism and regulation of copper homeostasis [94]. The genetic screenings have identified the genes that are responsible for Cu uptake under nutritional conditions, as well as for Cu distribution to the appropriate subcellular compartments and detoxification processes that are activated under toxic conditions, when Cu ions are present in excess [84]. In *S. cerevisiae*, copper is a cofactor of Cu/Zn-superoxide dismutase, cytochrome c oxidase (Cyt Ox), and of the FET3 and FET5 multicopper oxidases that are required for the several essential biochemical processes.

The copper uptake in this model microorganism is mediated by two separate systems: the so-called high-affinity system is involved under conditions of Cu nutritional depletion, while the low-affinity system operates in the presence of an excess of Cu ions, under toxic conditions [84, 94, 95].

The high-affinity copper uptake system involves two plasma membrane reductase enzymes, named Fre1 and Fre2, capable of inducing reduction of Cu^{2+} to Cu^{1+} and two high-affinity transporter proteins, Ctr1 and Ctr3, which operate on cuprous ions [84, 94, 96, 97].

The FRE1, FRE7, CTR1, and CTR3 species are downregulated by the transcriptional factor Mac1 [98–100] that is localized within the nucleus, apart from Cu^{1+} concentration in the cell, and is characterized by the cystein-rich carboxyterminal moieties with transactivation capability. Interestingly, Mac1 itself behaves as a Cu sensor, as its functioning may be repressed when Cu binds to its activation domain [94, 98]. The excess of Cu^{2+} ions induces the expression of genes that encode the proteins with a protective role, such as metallothioneins Cup1, Crs5, and superoxide dismutase Sod1. The expressions of *CUP1, CRS5,* and *SOD1* genes are activated by the transcription factor Ace1 [101].

The protein Ace1 cooperatively binds Cu^{1+} to form a tetra-Cu cluster through the specific cysteine residues within the amino-terminal DNA binding domain [84, 101, 102]. Copper binding leads to a conformational change in this domain resulting in the specific binding of Ace1 to the metal response elements (MREs) 5′-TCY(4-6)GCTG-3′ on the gene promoters involved in the copper detoxification and protection against oxidative damage [84, 103].

Three low-molecular-weight proteins have been identified, Cu-chaperone Atx1, Cox17, and Lys7, that are essential for the intracellular delivering of the Cu^{1+} ions to the cellular compartments. At least, one additional chaperone is expected to direct the Cu^{1+} ions to the nucleus for the regulation of Mac1 and Ace1 activities. These proteins bind copper after it enters the cell and subsequently deliver it to the corresponding recipient proteins. Atx1 is a small protein containing one metal-binding site and is the specific copper chaperone asked for copper delivering to the Ccc2 P-type ATPase in a late Golgi vesicle for the incorporation into Fet3 [95, 104, 105]. Cox17 is the copper chaperone that delivers copper to the mitochondria for Cyt Ox [106], while Lys7 is required to incorporate copper into Sod1 [107].

2.3 Zinc oxide: history and mechanisms of action

The first practice of zinc oxide is hardly traceable. Several zinc compounds were used by the early humans in various processed and unprocessed forms, but their exact composition is uncertain. Probably, it was used as a comfort for the eyes and wounds in India (500 BC or before) [108]. Zinc oxide cream is also mentioned by the Greek physician Dioscorides (1st century AD) [109]. Avicenna has introduced it in “The Canon of Medicine” (1025 AD), as a preferred treatment for a selection of skin conditions. It is still widely used to treat skin harms in products like baby powder and creams.

To the best of the authors’ knowledge, the efficiency of ZnO NP in imparting an antibacterial effect to the fabric is not yet well established, although it is known to strongly resist microorganisms [110–112]. The ZnO NPs are currently being investigated as an antibacterial agent both against the Gram-negative microorganism, such as *E. coli*, and Gram-positive microorganism such as *S. aureus* in the microscale and nanoscale formulations [113]. An important aspect of the use of ZnO as an antibacterial agent is the requirement that the particles are not toxic to the human cells [64, 114, 115].

Although the exact mechanism has not yet been clearly elucidated, the suggested mechanisms include the role of the ROS generated on the surface of the particle [113, 116–119], zinc ions release [120], membrane dysfunction [120, 121], and NP internalization [122]. The zinc ion sensors and regulatory mechanisms that control

homeostasis in *S. cerevisiae* are similar to those described in the case of copper [95].

3 Textile fibers modified with metal nanostructures

The smart and multifunctional textiles are one of the most promising fields, responding to the ever-growing demand for high-technology goods. The development of the novel antimicrobial textiles is receiving great impulse, due to the demand for increased hygienic conditions and for specific devices contributing to prevent the spread of pandemic diseases. Many commercial antibacterial textiles have been, so far, based on the molecular active agents, such as antibiotics, disinfectants, etc. [10, 123, 124].

In the following, we will focus on the use of the most important inorganic nanoantimicrobials (namely, Ag, Cu, ZnO) for such an application.

The different synthesis routes to modify the textiles are reviewed in the following subsections and classified as a function of the fiber composition (e.g., natural or synthetic).

3.1 Silver modified textile fibers

As the antimicrobial spectrum of silver is exceptionally broad against fungi [125], viruses [126–128], and bacteria [129] as well as the resistance of the pathogenic bacteria vs. many antibiotics is increasing, the growing interest in nanotechnologies and nanosized materials have led to a renewed interest into the silver-modified goods, mainly based on the AgNPs, for many applications [130], such as coatings for medical devices or textile [131–133], silver-coated textile fabrics [134], water sanitization [135], and so on. Consequently, various methods, depending on the particular active agent and fiber type, have been studied to give antimicrobial activity to the textiles.

3.2 Natural fibers

Among the natural fibers, the cotton textile was often selected for silver deposition because it represents a suitable substrate for both the common and medical clothing. For example, a method particularly indicated for the hospital uniforms and wound dressings has been studied by Gittard et al. [136] using a supercritical carbon dioxide solvent, which may be used to produce the cotton fiber textiles with uniform silver NP coatings.

The polymer-silver nanocomposite-modified cotton fabrics were prepared by *in situ* chemical oxidative polymerization using pyrrole and silver nitrate by Babu et al. [137]. In the proposed redox reaction, the silver ions oxidize the pyrrole monomer and undergo reduction. The antimicrobial activity of the Ag/polypyrrole-modified fabrics was tested against *S. aureus* and *E. coli*.

Another method for the cotton modification is the sol-gel technique for preparing the bioactive materials for biomedical applications [138]. The sol-gel coating of the cellulose fibers with antimicrobial and repellent properties have been also investigated by Tomšič et al.: multifunctional, water and oil repellent, and antimicrobial finishes for the cotton fibers were prepared from a commercially available fluoroalkyl functional water-born siloxane, nanosized silver and a reactive organic-inorganic binder. Two different procedures were used and physical as well as antibacterial tests were carried out [139].

Nanosilver oxide (nano-Ag-oxide) was *in situ* synthesized and deposited into cotton gauze fabrics by the reduction of silver nitrate solutions by Gouda [140]. The antibacterial activity of the prepared samples was evaluated using a reduction rate% in the bacterial count against *Salmonella typhimurium* and *S. aureus*, while antifungal activity was evaluated according to the clear inhibition zone diameter against *Candida albicans* and *Aspergillus flavus*. All the samples were durable toward washing and bioactive even after 30 laundering wash cycles.

The electron beam radiation was applied to synthesize the silver nanostructures in the cotton fibers by Zang et al. [141]. Investigations of the influence of the initial silver salt concentration on the size and distribution of the obtained silver nanostructures were carried out. The antibacterial activity of the Ag-cotton nanocomposites was evaluated as well.

In another paper, the cotton fabric was exposed to laser at different energy levels, and then, the silver NPs were coated on untreated and laser-treated cotton fabrics to determine the antibacterial activity [142].

The antimicrobial coatings for the textile based on AgCl in a silica matrix on cotton fabric have been developed by Tomšič et al. [143]. Also, the influence of the antimicrobial activity of the two contemporary finishes was studied by the same research group [144], specifically, a dispersion of colloidal silver and 3-(trimet hoxysilyl)-propyldimethyloctadecyl ammonium chloride (Si -QAC), on the degree of biodeterioration of 100% cotton and cotton/polyester hybrid fabric. Ag was chosen as the release

agent, while Si-QAC was used as the biobarrier-forming agent. The Ag agent can efficiently inhibit the biodeterioration of the cellulose fibers in the cotton and cotton/polyester fabrics, while the antimicrobial activity of Si-QAC was unsatisfying.

Tang and coworkers reported the combining of the silica and silver NPs on the surface of the wool fabrics [145]. The treated fibers with the silica and silver NPs showed a marked antibacterial activity because of the presence of the silver NPs.

The silver chloride nanocrystals have been synthesized on the silk fibers by sequential dipping in $AgNO_3$ and NaCl, pointing out the antibacterial properties of the resulting material [146]. The antibacterial efficiency of Ag/SiO_2 grafted on wool has been investigated by Wang et al. [147].

Nanosilver colloidal solution having the Ag/S complex has also been used by Ki et al. [148] for the functionalization of wool. Park et al. [149] developed an antimicrobial active robust metal-cellulose nanohybrid by the covalent assembly of the metal NPs on the cellulose fabric using a simple impregnation of the thiol-modified cellulose fabric in the colloidal silver NP solutions. This robust covalent linkage between the NPs and the fabric leads to a remarkable suppression of the release of the metal NPs from the fabric. In addition, the metal-cellulose nanohybrids showed a high antimicrobial activity in excess of 99.9% growth inhibition of the microorganism.

The silver/sodium carboxymethyl cotton dressing has been designed for burn wound bandages [150]. Nischala et al. [151] synthesized the silica-silver core-shell particles by the one-pot chemical method. The optimum density of the Ag NPs was found as a compromise between the needs of obtaining a good antibacterial activity and suppressing the Ag-NP surface plasmon resonance (responsible for the color alterations induced by the core-shell particle on the textile substrate).

In addition to the most common methods, sonochemical synthesis was proposed by Perelshtein [17] and Hadad [152] for preparing the natural or synthetic fabrics and wool fibers, respectively.

The impregnation methods have been used by Zhang et al. to treat the cotton fabric with silver nanocolloids. In this case, the antimicrobial activity was maintained after being exposed to 20 consecutive home laundering conditions [26]. The same method was used by Kim et al. [153], soaking the cotton fabrics into the silver colloid/3-MPTMS solution. These treated fabrics were tested for washing fastness and showed reasonable and relatively enhanced durability than the pad-dry-cure process, showing also an excellent antimicrobial performance.

Hebeish et al. have prepared the nanosilver colloidal solutions with a new copolymer, β-cyclodextrin grafted with polyacrylic acid using potassium persulfate as the initiator. The silver NP colloidal solutions were applied to the cotton fabric, showing excellent and durable antibacterial properties [154]. Also, Hebeish [155] showed the preparation of the AgNP solution using the environmental benign polymer (hydroxypropyl starch), which plays an important dual rule as both the reducing agent for Ag and stabilizer for the aqueous AgNPs. In addition, this kind of treatment was proposed as a safe, cost-effective, and environmental-friendly process in the fabrication of the antibacterial finishing and textiles.

A new approach to color and functionalize the conventional textile materials has been recently proposed by Tang et al. [156] assembling the anisotropic silver NPs on the wool fibers by the electrostatic interaction between the wool fibers and silver NPs. The modified wool fabrics exhibited brilliant colors due to the localized surface plasmon resonance (LSPR) properties of the silver NPs and antibacterial properties (see Figure 1). The surface plasmon resonance effect of silver has been used to color the merino wool fibers as well as impart the antimicrobial and antistatic properties by Kelly and Johnson [157]. The simultaneous antimicrobial properties and dyeing of the wool yarns were also achieved by Rad et al. [158], using a colloidal nanosilver solution and acid dye through an exhaustion method. The influence of the reactive dyes with massive chromogene and nanosilver on ultraviolet protective factor values of lightweight cotton fabrics was also investigated [159].

A novel method was introduced by Hosseinkhani et al. [160] in the textile processing to modify the coarse wool fineness along with the synthesis of nanosilver. Two different reducing agents with various concentrations were employed with different concentrations of the silver nitrate solutions. Further, the antibacterial properties of the fine wool were confirmed through testing with *S. aureus* and *E. coli*.

In a study by Sannino and coworkers [161], an innovative technique for the deposition of the nanosilver antibacterial coating on the woolen fiber was described. In particular, the fabrics woven with the different percentages of the silver-treated fibers were compared. The optimal mixing ratios, preserving the antibacterial activity and optimizing the cost-effectiveness of the final product were proposed. A very intense antibacterial activity against *E. coli* was found, even for the samples modified with a relatively low silver content.

El-Rafie et al. prepared the silver NPs colloid by making use of the biomass filtrate of the fungus *Fusarium*

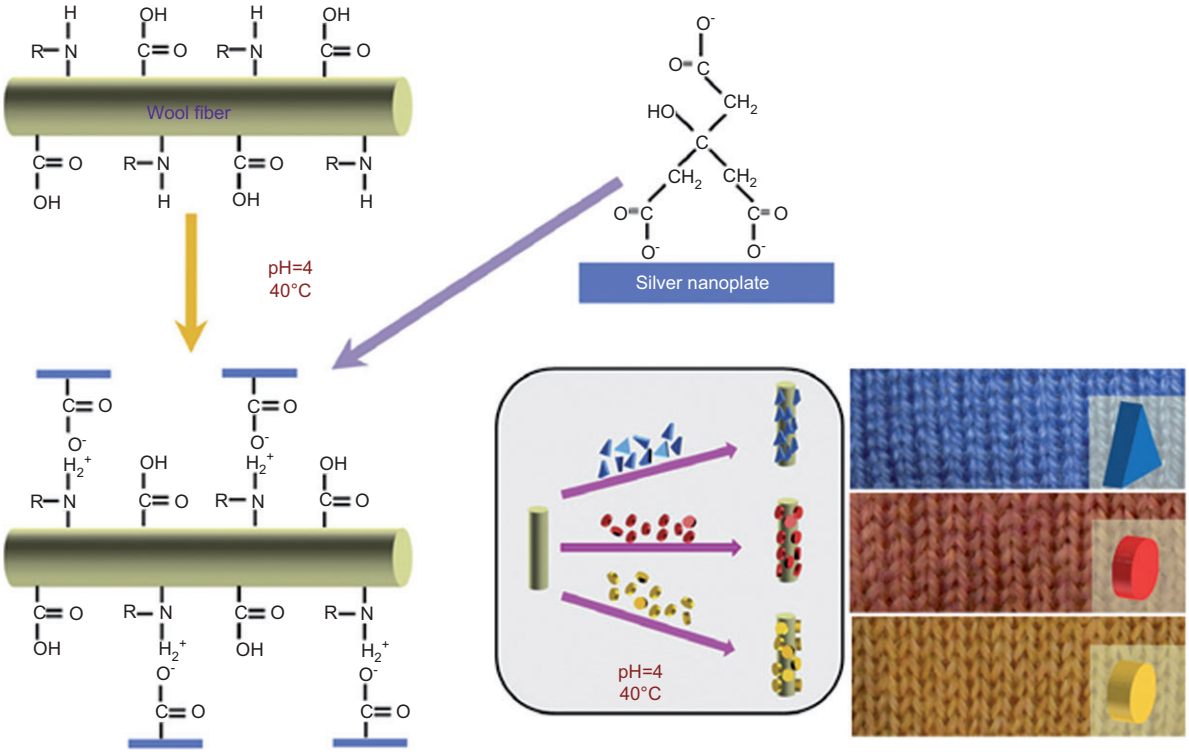

Figure 1 Coloration of wool fiber by using different silver NPs: (A) nanoprism I, (B) nanodisk I, and (C) nanodisk II. Reprinted from J. Colloidal Interface Sci., 2011, vol. 356, Tang B, Wang J, Xu S, Afrin T, Xu W, Sun L, Wang X, Application of anisotropic silver nanoparticles: multifunctionalization of wool fabric, pages 513–518. Copyright (2011), with permission from Elsevier.

solani. The finishing formulation containing as low as 54 ppm of the nanosilver particles were prepared and applied to the cotton fabrics with and without a binder [162].

A "green process" using the natural extracts of *Eucalyptus citriodora* and *Ficus bengalensis* has been studied by Ravindra et al. The results showed an excellent antibacterial activity by the incorporation of 2% leaf extracts on the cotton fibers even after several washings, indicating their usage in medical and infection-prevention applications [163]. Another ecological and viable approach for the *in situ* forming of AgNPs on the cotton fabrics has been used lately by El-Shishtawy et al., who employed silver nitrate, cetyl trimethyl ammonium bromide, Triton X-100, glucose, and sodium hydroxide. The presence of a low-coating level of nanosilver was shown to be enough for producing an excellent and durable antimicrobial effect in the cotton fabrics [164]. The natural, biocompatible, and biodegradable polysaccharide chitosan continues to be used, thanks to its excellent chelating property. The silver NP-loaded chitosan-attached cotton fabric exhibits an excellent antibacterial action against the model bacteria *E. coli* [165]. A biological method based on the extracellular reduction induced by *Fusarium oxysporum* was proposed by Durán et al. [166] to synthesize the silver NPs and cotton fabrics incorporated with these silver NPs that exhibited an antibacterial activity against *S. aureus*.

Falletta et al. have functionalized cotton, wool, and polyester samples in order to obtain the antimicrobial textiles for the biomedical applications. They synthesized silver-poly(acrylate) clusters in water by the reduction of $AgNO_3$ in the presence of poly(acrylates) of the different molecular weights through two different methods, $NaBH_4$ reduction and UV exposure [167].

Also, the plasma coatings can be used as permanent hydrophilic treatment or for substrate-independent dyeing when deposited on the textile fabrics. For instance, Hegemann et al. [168] studied plasma polymerization of acetylene mixed with ammonia. Using plasma cosputtering of a silver target, the Ag nanoparticles could be *in situ* embedded within the growing plasma polymer yielding a well-defined size and distribution of the nanoparticles at the coating surface.

In addition, the possibility to combine the antimicrobial treatment of the silver NPs with the conventional finishing processes has been studied by Khoddami et al. [169]. Fixapret® ECO as a crosslinking agent and Cellofix®

ME as a resin former have been used in anticrease finishing of the cotton fabric. The results showed that the treated samples by the pad-dry method have the best antibacterial effect, but washing and abrasion fastness were not at the acceptable level. Subsequently, they concluded that the antibacterial finishing method should be selected according to the end uses.

In a paper by Aly and coworkers [170], the multifinishing treatment of the cotton fabrics was carried out using the core-shell NPs that consist of the silver NPs as the core and chitosan-O-methoxy polyethylene glycol as the shell. The synthesized core-shell NP was applied to the cotton fabrics using the conventional pad-dry-cure method. The treated fabrics, at an optimum condition of 1% core shell NPs, 5% citric acid, drying at 80°C, and curing at 160°C for 2 min, showed an excellent antibacterial activity against *E. coli* and *S. aureus*, even after 20 washing cycles.

A pad-dry-cure process to obtain the treated fabrics was also carried out by Koparal and coworkers [171]. In this work, an antibacterial finishing agent containing calcium phosphate-based silver-doped powder was developed for the functionalization of the textiles and applied to 100% cotton and 100% polyester-knitted fabric samples. First, the silver-doped antibacterial powder was synthesized by using a wet chemical method; then, a size reduction process was applied for reducing the particle size from the micron size to the submicron scale. The treated fabrics were washed 20 times, and the antibacterial efficiency was evaluated according to the JIS-L 1902:2002 method against *E. coli*.

Mejía et al. [172] used magnetron sputtering to produce the cotton-Ag composites. A very peculiar case of the study is Abbasi et al.'s work [173], where the silver NPs have been used on the ancient textile to save it from demolition, decay, and damage.

Khalil-Abad and Yazdanshenas [174] and Xue et al. [175] have both studied the methods to prepare the superhydrophobic and antibacterial cotton textiles with a potential wide variety of biomedical and general use applications.

Sastri et al. [176] synthesized the silver NPs chemically by the wet reduction method and biologically by using the neem (*Azadirachta indica*) leaves. The coating of the socks fabrics (nylon and cotton) was carried out by exposing these fabrics to the prepared NP solutions on a gyratory shaker overnight. The antimicrobial activity of both the Ag-NP samples was carried out by performing minimum inhibitory concentration (MIC) and disc diffusion test against *Sarcina lutea*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *S. aureus*, and *Candida albicans*.

3.2.1 Synthetic fibers

For the synthetic fibers, the antimicrobial active agents can be incorporated into the polymer prior to the extrusion or blended into the fibers during their formation and during the melt spinning. There are numerous ways by which the antimicrobial properties can be accomplished in the textiles: the incorporation of the volatile and nonvolatile antimicrobial agents directly into the fibers, coating or adsorbing the antimicrobials onto the fiber surfaces, immobilization of the antimicrobials to the fibers by the ion or covalent linkages, and the use of fibers that are inherently antimicrobial [177].

The silver NPs are used on the synthetic textiles too: Dubas et al. immobilized them on the nylon (and silk) fibers, using the layer-by-layer deposition method and obtaining the colored thin film with the antimicrobial properties [178].

Very recently, a facile procedure for binding the silver NPs on the polyester fabrics was reported by Xu et al. [179]. In this paper, the multifunctional polymer films were first formed through the simple dip-coating of the polyester fabrics in an aqueous solution of dopamine. Then, the silver NPs were *in situ* generated on the surface of the dopamine-modified polyester fabrics in an aqueous solution of silver nitrate, at room temperature. The resulting fabrics loaded with the silver NPs showed a durable antibacterial activity.

The use of Si was studied by Mahltig with Textor [180] and Fisher [181] too: the SiO_2 coatings and inorganic/organic polymer hybrid coatings were applied onto the textiles on the synthetic fibers (polyamide and viscose). Silver was used for antimicrobial functionalization, and it was shown that the Ag release and the subsequent biocidal effect could be controlled by changing the metal content. To produce the commercial silver-coated nylon fabrics, 12% by weight of silver was added during manufacturing by an electroless plating process [182], and the antimicrobial capability of the nylon substrates coated with metallic silver has been checked against *P. aeruginosa*, *S. aureus* and *C. albicans* [183]. Magnetron sputtering has been also used to produce the silver-coated polyester fiber by Jiang et al. [184, 185].

Abbasi with Azadbakht reported on the novel synthesis of the acrylic fibers containing the Ag NPs under ultrasound irradiation [186]. The textile containing the NPs was successfully tested for their antibacterial efficacy against *E. coli* and *S. aureus*.

Perelshtein et al. described a process carried out by ultrasound radiation in a one-step reaction procedure to obtain both, synthetic (nylon and polyester) and natural (cotton), textiles with the antibacterial properties [17].

Besides, Ilić et al. [187] have described the antifungal efficiency of the pretreated polyester and polyamide fabrics treated with the Ag nanoparticles.

The durable antibacterial Ag/polyacrylonitrile hybrid nanofibers were prepared by the atmospheric plasma treatment and electrospinning by Shi et al. [188]. The hybrid nanofibers exhibited a slow and long-lasting silver ion release, which provided a robust antibacterial activity.

The highly hydrophilic fibers loaded with silver NPs were synthesized by an alternative approach, the electrospinning method [189]. First, poly (acrylic acid) and beta-cyclodextrin submicron fibers were electrospun; then, the silver ions were loaded into the fibers and reduced to silver NPs *in situ* (see Figure 2). These fiber mats show 99.99% of the killing efficiency, which is very attractive for the applications like wound healing and skin regeneration processes. To the best of the authors' knowledge, this is the first time that the stable hydrogel fibers with a highly biocide behavior have been fabricated using electrospinning.

In a work of Gawish et al. [190], the polypropylene/Ag composite fibers were produced by the melt-spinning method, and the antibacterial efficacy was evaluated by the percentage count reduction growth of *S. aureus* and *E. coli*.

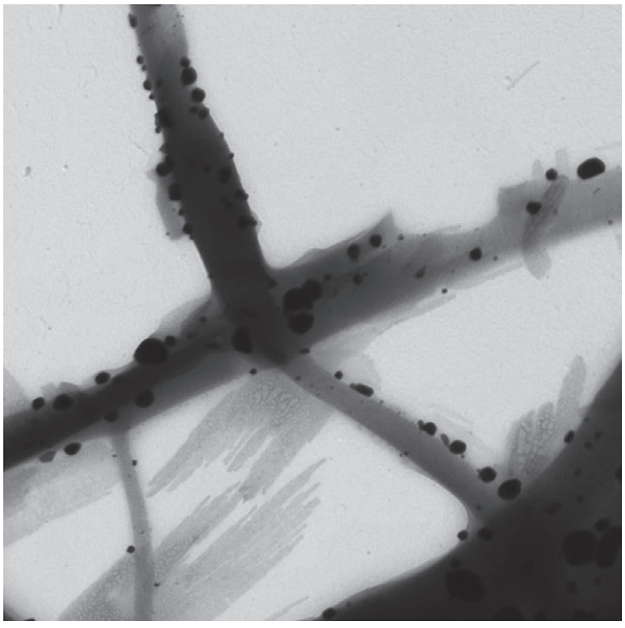

Figure 2 TEM image of Ag NP-loaded electrospun fiber mat. Reprinted from J. Appl. Polym. Sci., 2012, vol. 126. Rivero PJ, Urrutia A, Goicoechea J, Rodríguez Y, Corres JM, Arregui FJ, Matías IR, An antibacterial submicron fiber mat with in situ synthesized silver nanoparticles, pages 1228–1235. Copyright (2012), with permission from Wiley.

Owing to their high capacity, the nonwoven textiles have been used for a long time as potential filters to remove the harmful air pollutants. In a study by Khosravi and coworkers [191], the needle-punch polypropylene layers were treated with the nanosilver particle through the spray technique. *Staphylococcus aureus* and *E. coli* were completely removed from the passing air by the nanosilver-coated layer.

Kiwi and coworkers [192] obtained the uniform nanoparticulate Ag-thin films on the polyester textiles by the direct current (DC)-magnetron sputtering and pulsed DC-magnetron sputtering. The deposition of Ag on the polyester fiber and the bioactivity of the resulting material were observed to be dependent on the type of the sputtering used.

3.3 Copper modified textile fibers

Different synthesis [193, 194] and modification methods for the antimicrobial fabrics involving copper have been proposed in the last years [195]. In the following, several studies are reported and classified on the basis of the natural or synthetic character of the fibers.

3.3.1 Natural fibers

In a recent work, Anita et al. have prepared the copper oxide NPs by a wet chemical method using copper sulfate and sodium hydroxide as the precursors and soluble starch as stabilizing agent [43]. In the first step, the copper oxide NPs were microencapsulated by an ionic gelation method and applied to plain weave cotton fabric by exhaustion, then, in the second step by the pad-dry-cure method. The antibacterial efficacy of the copper oxide-encapsulated coated fabric was determined against *S. aureus* and *E. coli*. The authors suggested their employment in the manufacture of medical apparel.

Two works by Kiwi and coworkers [196, 197] addressed unreported features for Cu DC-magnetron sputtering on cotton. They dealt with the preparation and the characterization of CuO, the adhesion of the nanoparticulate CuO on the cotton activated by the RF plasma in comparison with the nonplasma-activated surfaces and the evaluation of *E. coli* inactivation by cotton/CuO in the dark and under light.

Osorio-Vargas et al. [198] have functionalized the Cu-cotton fabrics by the bipolar asymmetric DC-pulse magnetron sputtering (DCP). The *E. coli* inactivation was observed within 10 min when Cu was sputtered on the

cotton Cu for 60 s. The X-ray photoelectron spectroscopy (XPS) was used to determine the surface atomic concentration of O, Cu, C, and N along the copper speciation during the redox process leading to the *E. coli* inactivation.

Perelshtein et al. [199] produced the copper oxide NPs synthesized and deposited on the surface of the cotton fabrics by ultrasound irradiation. The process was proposed as a simple and efficient one-step synthesis. The homogeneous distribution of the CuO nanocrystals, 15 nm in size, on the fabric surface was obtained. The antibacterial activity of the CuO-fabric composite was tested, and a significant bactericidal effect, even in a 1% coated fabric (%wt), was found. The application of the coated fabrics was envisaged in wound dressings, bed linings, and as active bandages.

An interesting pilot installation for the scale up of the sonochemically assisted coating of the textile fabrics with the various kinds of NPs was proposed by Abramov et al. [200]. The installation could coat up to 50 m of the continuous cotton fabric per run with CuO or ZnO NPs. The coating was homogeneous, stable, and retained its biocidal properties through at least 20 washing cycles. The CuO-cotton bandages demonstrated good antimicrobial properties against *Escherichia coli* (see Figure 3).

Chattopadhyay and Patel [201] produced the copper nanocolloids prepared by the chemical reduction of copper salt using sodium borohydride in the presence of trisodium citrate. The results of the particle size analysis showed that the average particle size varied from 60 to 100 nm. The treatments of the nanocopper colloidal solution on the cotton improved its antimicrobial efficiency (soil burial test) and also influenced the tensile strength of the fabric sample positively.

The synthesis of the copper alginate-cotton cellulose (CACC) composite fibers were proposed by Grace et al. [202]. The CACC fibers were prepared by immersing the cotton fibers in aqueous solution of sodium alginate, followed by the ionic crosslinking of the alginate chains within the cotton cellulose fibers with Cu(II) ions. Finally, the CACC fibers were reduced by sodium borohydride to yield the copper NP-loaded composite fibers and investigated for biocidal action toward *E. coli*. It was found that the CACC fibers possessed both the fair mechanical strength and antibacterial action. The authors suggested these fibers have great potential as dressing materials. Another work of Grace et al. [203] described the release of copper(II) ions from the cellulose fibers, which were chemically modified by periodate-induced oxidation of cellulose, followed by the covalent attachment of the biopolymer chitosan. The fibers showed an antibacterial activity against *E. coli*. In addition, the borohydride-induced reduction of these fibers also yields the copper NP-loaded fibers, which also possess fair antibacterial properties. In this case, the authors recommended these fibers to be used in burn/wound dressing and also in the fabrication of antibacterial dressing (see Figure 4).

Berendjchi et al. [204] discussed the synthesis of silica sol, doped with two different amounts (0.5% and 2% wt/wt) of the Cu NPs. The cotton fabric samples were impregnated by the prepared sols and tested successfully against *S. aureus* and *E. coli*.

In a work by Gabbay et al. [205], both the natural and synthetic fibers have been considered. The authors reported that the copper-impregnated fibers of the cotton and polyester containing 3–10%wt Cu had shown significant antifungal and antimicrobial properties. The biocidal characteristics were reported to be permanent, unaffected by extreme washing conditions, and they did not interfere with the processing of the final products (e.g., color, press, etc.).

In another work by Kiwi and coworkers [206], Cu DC-magnetron sputtering leads to the thin metallic semi-transparent gray-brown Cu coating composed of the Cu nanoparticulate in the nanometer range, as found by the electron microscopy. The DC-magnetron sputtering (DCMS) for 40 s of Cu on cotton inactivated the *E. coli* within 30 min under visible light and within 120 min in the dark. For a longer DCMS time of 180 s, the Cu content was ca. 0.3% w/w, but the bacterial inactivation kinetics under light was observed within 30 min, as was the case for the 40-s sputtered sample. The Cu ionic species were hypothesized to play a key role in the *E. coli* inactivation. The bioactive Cu was also deposited on the polyester in the form of Cu_2O and CuO, as shown by the XPS and antibacterial tests [206].

3.3.2 Synthetic fibers

The Cu polyester thin-sputtered layers on the textile fabrics showed an acceptable bacterial inactivation kinetics using the sputtering methods [206]. Recently, Rio et al. [207] tested the antimicrobial activity of the Cu-sputtered polyester surfaces, obtained by DC-magnetron sputtering, against methicillin-resistant *S. aureus* (MRSA). The Cu-polyester microstructure was characterized by the high-resolution transmission electron microscopy to determine the microstructure of the Cu NPs and by profilometry to assess the thickness of the layers. The sputtering at 300 mA for 160 s led to a Cu

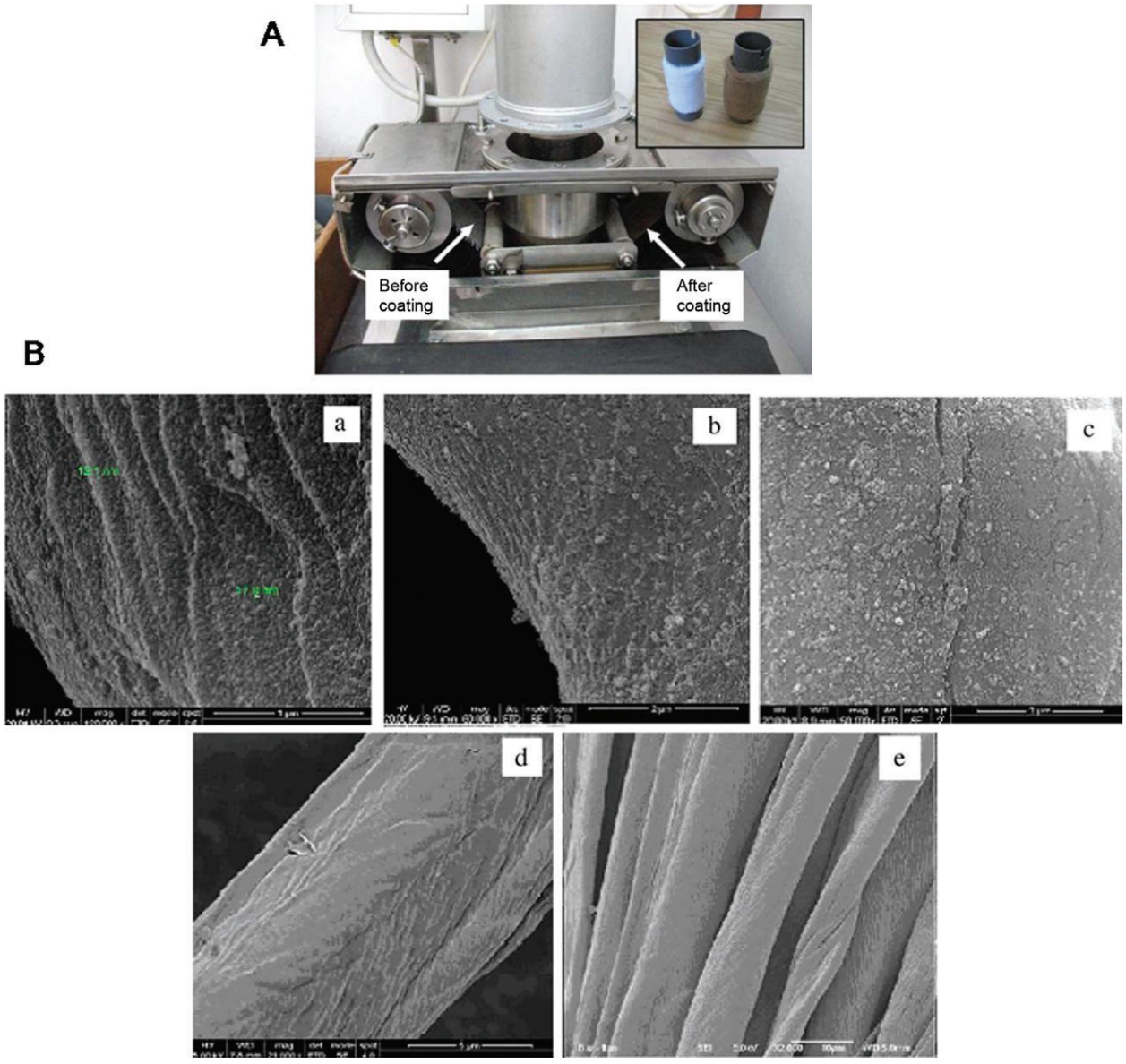

Figure 3 (A) Picture of the pilot installation described in Ref. [200]. In the inset, the CuO-coated and uncoated spools are shown. (B) HR SEM images of the CuO/cotton bandage prepared on the pilot installation from the 0.02-mol solution of Cu^{2+}: after 10 min of the reaction (a); after 40 min of the reaction (b); after 40 min of the reaction with the addition of 10% of the precursor to the working solution (c); the pristine uncoated cotton bandage (d), the cotton bandage after immersion in the slurry containing copper oxide without sonication (e). Reprinted from Surf. Coat. Technol., 2009, vol. 204, Abramov OV, Gedanken A, Koltypin Y, Perkas N, Perelshtein I, Joyce E, Mason TJ, Pilot scale sonochemical coating of nanoparticles onto textiles to produce biocidal fabrics, pages 718–722, Copyright (2009), with permission from Elsevier.

film thickness of 20 nm (100 Cu layers) containing 0.2% (wt/wt) polyester. The viability of the MRSA strain ATCC 43300 on the Cu-sputtered polyester was evaluated by four methods: mechanical detachment, microcalorimetry, direct transfer onto the plates, and stereomicroscopy. The low efficacy of the mechanical detachment impeded the bacterial viability estimations. The microcalorimetry provided only semiquantitative results. The direct transfer onto the plates and stereomicroscopy seemed to be the most suitable methods to evaluate the bacterial inactivation potential of the Cu-sputtered polyester surfaces, as they presented the least experimental bias. The Cu-polyester samples sputtered for 160 s were further tested against 10 clinical MRSA isolates and showed a high level of bactericidal activity, with a 4-log(10) reduction in the initial MRSA load [10(6) colony-forming units (CFUs)] within 1 h. The Cu-sputtered polyester surfaces might be useful to prevent the transmission of the health care-associated infection pathogens [207].

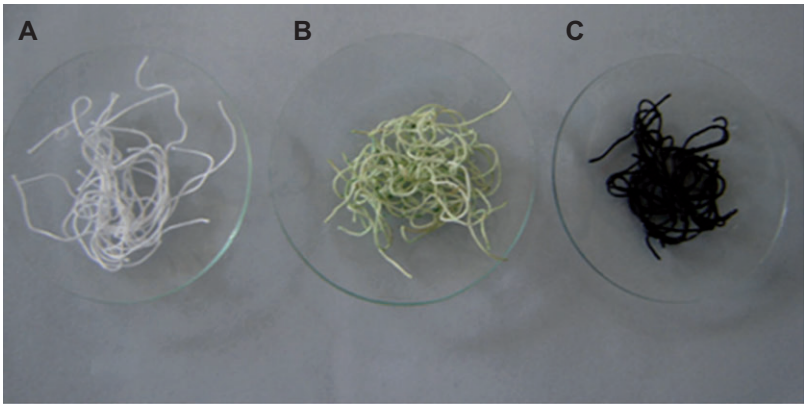

Figure 4 Picture showing plain cotton fibers (A), copper-bound chitosan-attached cellulose fibers (B), nanocopper loaded chitosan cotton fibers (C). Reprinted from J. Appl. Polym. Sci., 2009, vol. 11, Grace M, Bajpai SK, Chand N, Copper (II) ions and copper nanoparticles-loaded chemically modified cotton cellulose fibers with fair antibacterial properties, pages 757–766, Copyright (2009), with permission from Wiley.

3.4 Zinc oxide-modified textile fibers

The metal oxides such as TiO_2, ZnO, MgO, and CaO are of particular interest because of their stability under harsh process conditions and also generally regarded as safe materials to human beings and animals [199, 208].

In particular, ZnO is generally nontoxic, capable of photocatalytic oxidation, and chemically stable under exposure to high temperature [209]. Furthermore, the ZnO NPs have some advantages, compared to nano-Ag, too, such as lower cost, white color [210], and UV-blocking property [44, 211]. ZnO is also used to reinforce the polymeric bionanocomposites [211] and to enhance the wear-resistant phase and antisliding phase in the composites as a consequence of its high elastic modulus and strength [212].

3.4.1 Natural fibers

There are only a few methods, such as the pad-dry-cure method, radiation, and thermal treatments, that describe the coating of the ZnO NPs on the cotton fabric.

El Shafei and Abou-Okeil [213] focused their paper on the preparation and characterization of ZnO/carboxymethyl chitosan bionanocomposite (see Figure 5). The application of the bionanocomposite to the textile materials aimed at producing functional textiles by the pad-dry-cure method to impart UV and antibacterial activity to the cotton fabric. In another study from the same authors [108], the synthesis of the reactive preformed polymers (PFP) and their application to the cotton fabrics was

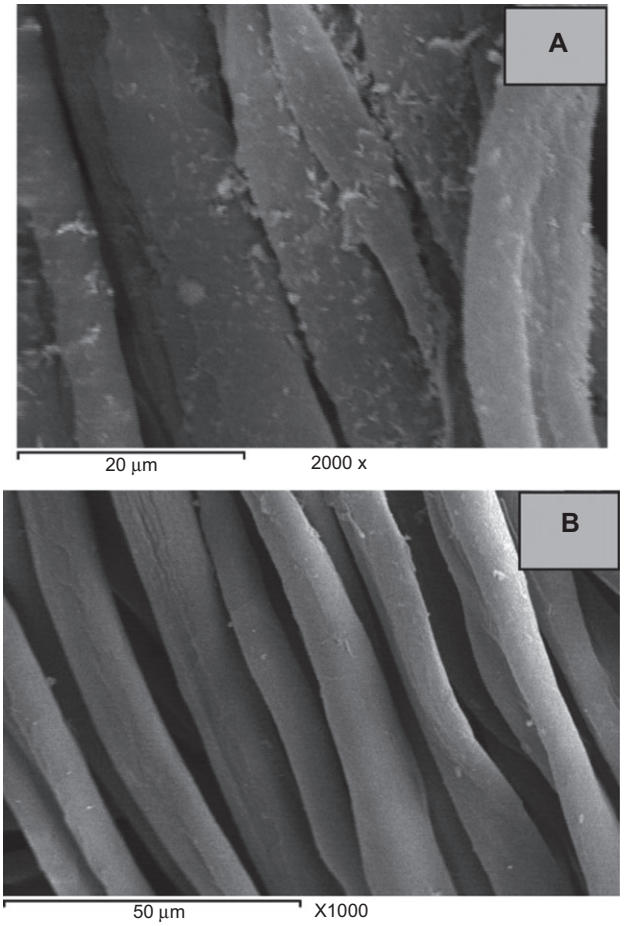

Figure 5 SEM pictures of the pristine cotton fabric (B) and cotton fabric treated (A) with ZnO/CMCTS bionanocomposite. Reprinted from Carbohydr. Polym., 2011, vol. 83, El Shafei A, Abou-Okeil A, ZnO/carboxymethyl chitosan bionano-composite to impart antibacterial and UV protection for cotton fabric. Pages 920–925, Copyright (2011), with permission from Elsevier.

proposed. The grafting of the PFP to the cotton fabrics in the presence of ZnO NPs and/or epichlorohydrin imparted an antibacterial activity to the substrates, which withstood 20 times of washing while keeping 70% of this activity.

Rajendran et al. [214] investigated the zinc oxide NPs prepared by the wet chemical method and directly applied on to the 100% cotton-woven fabric using the pad-dry-cure method. The antibacterial activity of the finished fabrics was studied, and their results showed that the finished fabric demonstrated a significant antibacterial activity against *S. aureus*. The wash durability study of the treated fabric was also carried out and found to withstand up to 25 wash cycles.

Selvam et al. [215] carried out the functionalization of the cotton fabric with poly-N-2-pyrrolidone (PVP) for improving the dyeability of the dichlorotriazine dyes, and subsequently, the ZnO NPs were coated by the pad-dry-cure method on the functionalized textiles. The PVP-modified cotton fabrics showed good dye uptake, color strength, and fastness properties for the three dichlorotriazine-reactive dyes. In the antibacterial tests against *S. aureus* and *E. coli*, the PVP/ZnO-modified fabrics showed very good bacterial reduction. These fabrics were proposed as wound cloths, surgical cloths, sportswear, and kids wear.

Li and coworker [216] have investigated the durability of the antibacterial activity of the nano-ZnO functionalized cotton fabric to sweat. The durability of the antibacterial activity of the finished fabric in alkaline, acidic, and inorganic salt artificial sweat solution was evaluated. The results showed better salt and alkaline resistances than acid resistances for the treated fabrics. A negative surface charge was deduced for the ZnO NPs, and it was envisaged that the illumination can increase the antibacterial performance.

The chalcones and ZnO flower-like nanorods were prepared and coated by Sivakamur et al. on the cotton cloth with acacia as the binder [217]. The antibacterial activity of the coated cotton was tested against *S. aureus*, *E. Coli*, and *P. aeruginosa* in terms of live bacterial load, as measured by the CFUs, adhered on the cotton surface. More than 99% reduction in bacterial load was observed toward all the three microorganisms.

Three shapes of the nano-ZnO were prepared and then applied on the cotton fabrics by Neamjan and coworkers [218]: ZnO multipetals, ZnO rods, and ZnO spherical particles. The as-prepared suspension was applied onto the cotton fabrics via the pad-dry-cure process at 150°C. All the treated samples showed good antibacterial activity against S. Aureus, but the shape of the ZnO particles showed a little effect on this activity.

Very recently, Subash et al. developed the NP-coated cotton fabric [219]. Zinc oxide NPs were prepared by the wet chemical method using zinc nitrate and sodium hydroxide. The antibacterial property of the treated fabric was analyzed. The results indicated that the 2% zinc oxide NP (200 nm)- coated fabric have a high antibacterial efficiency (99.9% against *S. aureus* and 80% against *E. coli*), and upon washing the coated fabric (five hand washes), the antibacterial activity was found to be 98% against *S. aureus* and 75% against *E. coli* [219].

Cakir et al. [220] provided a new method to impart the antimicrobial properties to the textile fabrics. The Zinc oxide (ZnO) NPs were synthesized in the reverse micelle cores of PS(10912)-b-PAA(3638) copolymer synthesized by the atom transfer radical polymerization at various precursor:copolymer ratios (10:1, 20:1, and 40:1). The size and morphology of the ZnO NPs were characterized via the TEM and XRD measurements. Then, the copolymer solution including the ZnO NPs was deposited onto the cotton fabrics to enhance the UV-blocking, self-cleaning, and antibacterial properties. In fact, the nano-ZnO-coated textile samples exhibited an antibacterial activity against *E. coli* and *S. aureus* (see Figure 6)

Finally, the immobilization of the ZnO NPs on the cotton fabrics using poly 4-styrenesulfonic acid (PSS) was studied by Iamphaojeen and Siriphannon [221]. The resulting immobilization of the ZnO nanocrystals on the cotton fabrics was investigated by SEM, XRF, and XPS. The ZnO-immobilized cotton fabrics inhibited the growth of *S. aureus*, as demonstrated by the AATCC 147-2004 standard test method.

3.4.2 Synthetic fibers

Among the publications regarding the ZnO-modified synthetic textiles, the ZnO-loaded polyamide 6 (PA6) nanocomposite fibers [222], ZnO modified polyester nonwoven fabrics [223], and polypropylene/nanometal composite fibers [190] are particularly interesting.

Skrifvars and coworkers [222] investigated the preparation of the PA6/ZnO nanocomposite fibers by the melt-spinning method. The nanocomposite fibers containing the ZnO NPs at four different loadings were prepared. The antibacterial activity of the fibers against *S. aureus* as a Gram-positive bacterium and *Klebsiella pneumoniae* as a Gram-negative bacterium was determined according to ASTM E 2149-0. It is found that the dispersion of the ZnO particles within the PA6 matrix is homogenous. The antibacterial activity tests showed that the PA6/ZnO nanocomposite fibers exhibit antibacterial efficiency

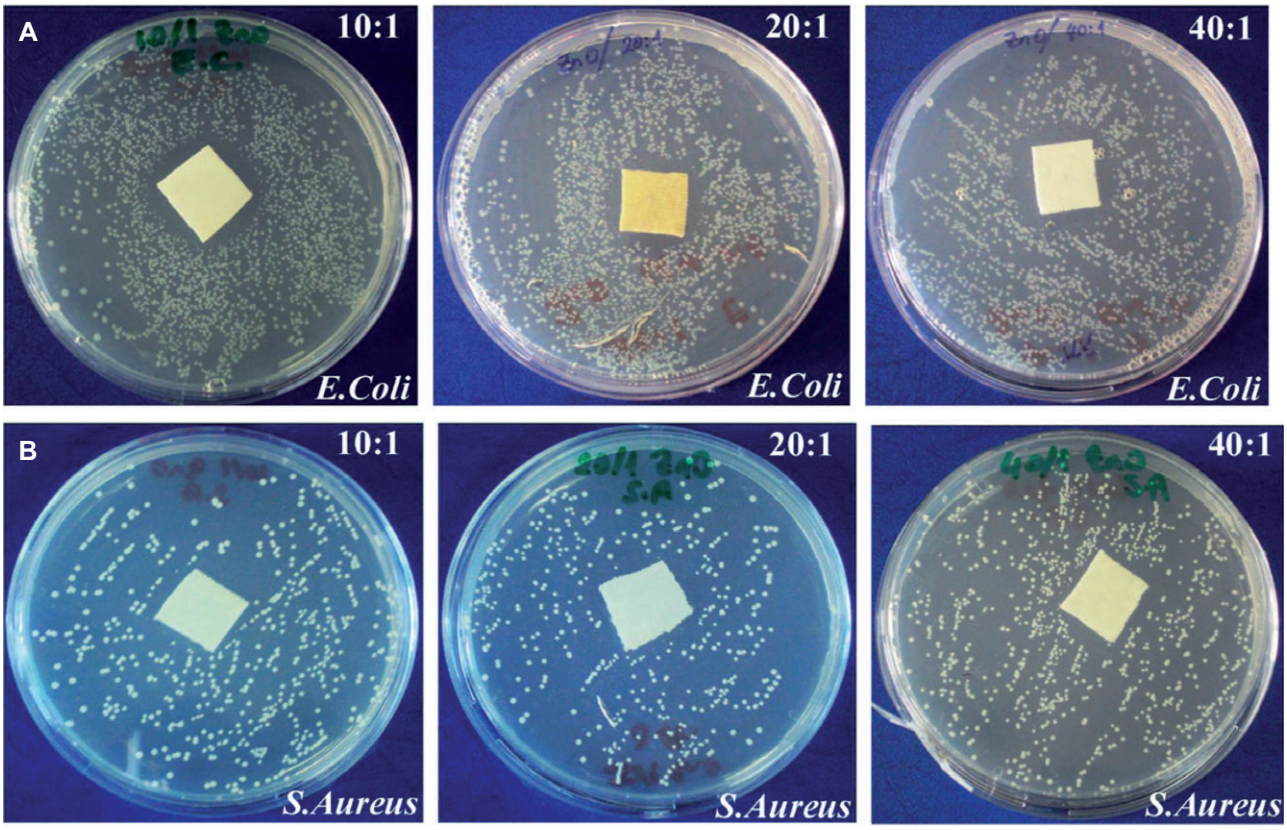

Figure 6 Antibacterial activities of the nanoZnO-coated textile samples with 10:1, 20:1, and 40:1 of the Zn^{+2}:copolymer ratio against *E. coli* (A) and *S. aureus* (B). Reprinted from Coll. Surf. A: Physicochem. Eng. Aspects., 2012, vol. 414, Cakir BA, Budama L, Topel O, Hoda N, Synthesis of ZnO nanoparticles using PS-b-PAA reverse micelle cores for UV protective, self-cleaning and antibacterial textile applications, pages 132–139, Copyright (2012), with permission from Elsevier.

related to their NP contents. An increase in the amount of the NPs caused an increase in the antibacterial activity of the fibers. These nanocomposite fibers were proposed for medical application, such as sutures and meshes.

Jesionowski et al. [223] synthesized ZnO by precipitation using the emulsion method, and then, the ZnO phases were deposited onto the polyester nonwoven fabrics. The antimicrobial properties of the modified textiles were evaluated against *S. aureus* and *E. coli* by the screening method according to PN-EN ISO20645, on the basis of the presence and size of the inhibition zone. The polyester nonwoven fabric modified with zinc oxide revealed a high antibacterial activity.

Finally, in the work of Gawish et al. [190], the PP/Zn composite fibers were produced by the melt-spinning method, and the antibacterial efficacy was evaluated by the percentage count reduction growth of *S. aureus* and *E. coli*. A metal content slightly higher than 0.1% was required to obtain a significant antibacterial activity, and the antibacterial efficacy of PP fibers increased by increasing the nanoantimicrobial content.

4 Modification methods for fabric applications

In the previous sections, we have reviewed several methods to modify the natural and synthetic fibers for improving their properties and, in particular, for providing antimicrobial activity. This paragraph is focused on the selected deposition techniques that are presently employed in our laboratories for the controlled modification of the textiles by the nanoantimicrobial inclusions. Three possible approaches are briefly discussed, e.g., the photoreduction of silver salts, ion beam sputtering deposition of metal-fluoropolymer nanocomposites, and electrochemical synthesis of metal nanoantimicrobial colloids.

4.1 Photoreduction of silver salt

An innovative technology to obtain the antibacterial textile by silver particle deposition has been developed

and patented by Sannino and coworkers [224]. The technology, based on the photoreduction *in situ* of a silver salt, can be applied to many different types of substrate [225] and, in particular, it has been extensively studied, and it is being applied to textile, both natural and synthetic (wool, flax, cotton, polyester, nylon, etc.) [161, 226, 227]. The durable antibacterial textile for many applications was obtained, from the common knitwear or underwear treated with silver to guarantee a major welfare, to the hospital textile, where silver represents a promising instrument for advanced wound dressing [228] or antiseptic bandage [229].

The treatment consists of the deposition of a silver solution on the surface of substrate by spray coating or dip coating; then, the impregnated substrates are exposed to an ultraviolet source, like a UV lamp, in order to induce the photoreduction.

Usually, in this process, a silver salt, used as precursor of the metallic silver, is dissolved in methanol or in a mixture of methanol and water. The process, in which methanol is both the solvent and reducing agent, is based on the following chemical reaction:

$$Ag_n + 2Ag^+ + CH_3OH + h\upsilon => Ag_{n+2} + 2H^+ + CH_2O$$

The mentioned technology ensures that the silver particles remain firmly bonded to the substrate, and the antibacterial effect is permanent also after the several industrial washing cycles. The hypoallergenicity and the skin irritability of the antibacterial samples of the fabrics were verified by appropriate analysis carried by specialized laboratories.

4.2 Ion beam sputtering deposition of metal-fluoropolymer nanocomposites

Ion beam cosputtering (IBS) is a low-cost deposition technique, which is very versatile for the production of the thin metal-fluoropolymer nanostructured films, by means of a controlled inclusion of the metal NPs in a fluoropolymer (CF_x)-dispersing matrix.

The metal-fluoropolymer (Au-CF_x, Ag-CF_x, Pd-CF_x, Cu-CF_x) nanocomposites can be deposited at room temperature and at a pressure of 10^{-4} mbar on the different substrates by cosputtering a Teflon target and a metal one (Au, Ag, Pd, Cu) with Ar^+ ion beams.

The good reproducibility of the deposition experimental parameters (ion-beam energy and current) allows the control of the growth rate of each component in the nanocomposite material and, therefore, the metal volume fraction value, which can range from 0 to 1.

The IBS results to be competitive with the other methods for the realization of the innovative textile products because it also allows for the multifunctional modification of textiles, with both antibacterial and dirt-repellent as well as water-repellent properties. A schematic diagram of the dual-beam IBS setup and more details of the deposition technique have been reported elsewhere [230–233].

The textile fibers coated with a sputtered metal-fluoropolymeric nanocomposite film show a challenging antibacterial activity. When left in contact with the culture broths of the target microorganisms, the IBS-treated fiber surface releases the metal ions included, which interact with bacteria (e.g., *E. coli*, *S. aureus*, etc.) inhibiting their growth into colonies. The extent of such antimicrobial properties depends on the metal loading in the composite.

A tuneable metal loading and, therefore, a tuneable metal ion release in solution, a very good stability toward storage and, most of all, a marked biostatic effect on the different target microorganisms strongly support the application of the metal-CFx coatings in the important fields such as food chemistry, biomedicine, and antibacterial textile.

4.3 Electrochemical synthesis of silver or copper nanoparticles

The sacrificial anode electrosynthesis of the metal NPs in the presence of the cationic surfactants is a simple and particularly versatile method, which allows to tune the particle size through simple parameters, such as the electrolysis potential [234].

The sacrificial anode electrolytic process was performed by using a tree-electrode cell, equipped with a bioactive metal sheet (copper, zinc, silver, etc.) as the anode electrode, a platinum sheet as the cathode electrode, and the proper reference electrode. During the process, when the applied potential is sufficiently high, the anode dissolves under the form of metal ions that are subsequently reduced at the cathode surface in the presence of proper surfactants, such as tetra-n-alkyl-ammonium salts, which stabilize the NP under the form of a core-shell structure in which the copper (or silver, or zinc oxide) core is surrounded by the quaternary ammonium ions. The surfactant is both used as the base electrolyte and as stabilizing agent, as it adsorbs on the surface of the metal clusters (produced by means of the cathodic reduction), thus, preventing their excessive growth and promoting their dissolution as the spherical NPs with high morphological stability [194, 235–238].

We have electrosynthesized several bioactive nanocolloids, which have been then used as modifiers of commercially available polymers and textiles. The peculiarity of these materials consists of the stabilized structure of the NPs, which allows a gradual and controlled copper ion release, when the nanocoating is exposed to aqueous solutions. The release extent of the bioactive ions is easily tuneable by a proper selection of the preparation parameters, such as the metal loading in the coating [239].

The nanostructured coatings are capable of releasing metal ions in a culture broth of living microorganisms in a concentration range that can be finely selected in order to be effective (e.g., biocide or biostatic) toward several target organisms [194, 235–238].

5 Conclusions and perspectives

A concise overview of technologies in use for the controlled inclusion/deposition of antimicrobial nanophases into textile goods has been provided in this paper. The referenced studies have been classified as a function of the composition of the nanoantimicrobial agent –herein, we have decided to focus on the most diffused ones, namely: copper-, silver-, and zinc oxide-based nanophases-, and as a function of natural/synthetic composition of the textile. Very short descriptions about the processes and nanomaterials developed in the authors laboratories have been provided, as well.

The large number of academic studies cited outlines the importance of this research field in real-life applications and usages. Interestingly, patented processes are attracting even a greater interest towards this field in recent years. The worldwide demand for "smart" products combining several properties, including efficient antibacterial activity, is stimulating the diffusion of real-life goods which do not employ conventional antibiotics. In this respect, using NPs as smart surface modifiers providing a controlled release of bioactive ions [239] can offer several advantages, preventing or limiting direct nanotoxicity and other undesired effects. Bioactivity patterns activated by NPs can be certainly more complex than just those based on ionic activity [240, 241], and concerns about nanotoxicology issues related to the use of the most common nanoantimicrobials have been risen by several authors [242]. Nevertheless, the number of patents on nanoantimicrobials-modified textiles is increasing and covers nowadays almost any combination of different metal(s), and kind of textile fiber [243–248]. Among the most promising directions for a further development of this field, the authors of this review envisage the development of nanoantimicrobials-modified nonwoven fabric [249], medical gauzes [250], wound dressing [247], wet-tissues [251] and other disposable goods for medical or health-care [252] purposes.

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References

[1] Vigo TL, Benjaminson MA. Antibacterial fibre treatment and disinfection. *Text. Res. J.* 1981, 51, 454–465.
[2] Yang JM, Lin HT, Wu TH, Chen CC. Wettability and antibacterial assessment of chitosan containing radiation-induced nonwoven fabric of polypropylene-g-acrylic acid. *J. Appl. Polym. Sci.* 2003, 90, 1331–1336.
[3] Younsook S, Dong Y, Kyunghye M. Antimicrobial finishing of polypropylene nonwoven fabric by treatment with chitosan oligomer. *J. Appl. Polym. Sci.* 1999, 74, 2911–2916.
[4] Macken C. Bioactive fibres – benefits to mankind. *Chem. Fibers Int.* 2003, 53, 39.
[5] Gao Y, Cranston R. Recent advanced in antimicrobial treatments of textiles. *Text. Res. J.* 2008, 78, 60–72.
[6] Jiannming J, Yumei Z, Meifang ZY, Meifang Z. Structure of antimicrobial polypropylene fibre. *J. China Text. Univ.* 1997, 14, 41–46.
[7] Mosleh S, Gawish SM, Sun Y. Characteristic properties of polypropylene cationic fabrics and their derivatives. *J. Appl. Polym. Sci.* 2003, 89, 2917–2922.
[8] Kim YH, Sun G. Durable antimicrobial finishing of nylon fabrics with acid dyes and a quaternary ammonium salt. *Text. Res. J.* 2001, 71, 318–323.
[9] Ladhari N, Baouab MHV, Dekhil AB, Bakhrouf A, Niquette P. Antibacterial activity of quaternary ammonium salt grafted cotton. *J. Text. Inst.* 2007, 98, 209–218.
[10] Dastjerdi R, Montazer M. A review on the application of inorganic nano-structured materials in the modification of

textiles: focus on anti-microbial properties. *Colloids Surf. B.* 2010, 79, 5–18.
[11] Marcincin A, Ujhelyiova A, Legen J, Kabatova V, Jambrich P. Bioactive polypropylene fibres. *Fibres Text.* 1997, 4, 38–43.
[12] Kim YH, Choi HM, Yoon JH. Synthesis of a quaternary ammonium derivative of chitosan and its application to a cotton antimicrobial finish. *Text. Res. J.* 1998, 68, 428–434.
[13] Mao L, Murphy L. Durable freshness for textiles. *AATCC Rev.* 2011, 28–31.
[14] Shalaby SE. Antimicrobial fabrics, *U. S. Pat. Appl.* 2004, 6, 780–799.
[15] Shima TN. Antibacterial activity of cellulose fabrics modified with metallic salt. *Text. Res. J.* 2001, 71, 688–694.
[16] Stevanato R, Tedesco R. New antimicrobial acrylic fibre. *Chem. Fib. Int.* 1998, 48, 480–485.
[17] Perelshtein I, Applerot G, Perkas N, Guibert G, Mikhailov S, Gedanken A. Sonochemical coating of silver nanoparticles on textile fabrics (nylon, 1558 polyester and cotton) and their antibacterial activity. *Nanotechnology* 2008, 19, 1–6.
[18] Pauqquet JR, Rzymelika PS. Novel effect additives for increasing versatility of synthetic fibres. *Chem. Fibers Int.* 2001, 51, 446–448.
[19] Cox R. Amicor – antimicrobial fibres. *Chem. Fibers Int.* 1998, 48, 486–489.
[20] Cox R. Re-positioning acrylic fibres for the new millennium. *Chem. Fibers Int.* 2001, 51, 118–128.
[21] Diz M, Infante MR, Erra P. Antimicrobial activity of wool treated with a new thiol cationic surfactant. *Text. Res. J.* 2001, 71, 695–700.
[22] Mansfield RG. Keeping it fresh. *Text. World*. 2002, 152, 42.
[23] Dunn RL, Gibson JW, Perkins BH, Goodson J, Laufe MLB. Fibrous delivery systems for antimicrobial agents. *ASC-Polym. Mater.: Sci. Eng.* 1984, 51, 28–31.
[24] Seong HS, Kim JP, Ko SW. Preparing chito-oligosaccharides as antimicrobial agent for cotton. *Text. Res. J.* 1999, 69, 483–488.
[25] Chapman K. High-tech fabrics for smart garments. *AATCC Review*. 2002, 2, 11–15.
[26] Zhang F, Wu X, Chen Y, Lin H. Application of silver nanoparticles to cotton fabric as an antibacterial textile finish. *Fibres Polym.* 2009, 10, 496–501.
[27] Ren XH, Kou L, Kocer HB, Zhu CY, Worley SD, Broughton RM, Huang TS. Antimicrobial coating of an N-halamine biocidal monomer on cotton fibres via admicellar polymerization. *Colloids Surf. A.* 2008,317, 711–716.
[28] Dastjerdi R, Montazer M, Shahsavan S. A new method to stabilize nanoparticles on textile surfaces. *Colloids Surf. A.* 2009, 345, 202–210.
[29] Dastjerdi R, Mojtahedi MRM, Shoshtari AM, Khosroshahi A. Investigating the production and properties of Ag/TiO_2/PP antibacterial nanocomposite filament yarns. *J. Text. Inst.* 2010, 101, 204–213.
[30] Hasebe Y, Kuwahara K, Tokunaga S. Chitosan hybrid deodorant agent for finishing textiles. *AATCC-Rev.* 2001, 1, 23–27.
[31] Kobayashi Y, Nakanishi T, Komiyama J. Deodorant properties of wool fabrics dyed with acid mordant dyes and a copper salt. *Text. Res. J.* 2002, 72, 125–131.
[32] Payne J. From medical textiles to smell-free socks. *J. Soc. Dyers Colour.* 1997, 113, 48–50.
[33] Borkow G, Gabbay J. Biocidal textiles can help fight nosocomial infections. *Med. Hypotheses* 2008, 70, 990–994.
[34] Bagherzadeh R, Montazer M, Latifi M, Sheikhzadeh M, Sattari M. Evaluation of comfort properties of polyester knitted spacer fabrics finished with water repellent and antimicrobial agents. *Fibres Polym*. 2007, 8, 386–392.
[35] Montazer M, Afjeh MG. Simultaneous x-linking and antimicrobial finishing of cotton fabric. *J. Appl. Polym. Sci.* 2007, 103, 178–185.
[36] Edwards JV, Vigo TL, *Bioactive Fibres and Polymers*. American Chemical Society: Washington, DC. 2001.
[37] Kaushik P, Malik A. Fungal dye decolourization: recent advances and future potential. *Environ. Int.* 2009, 35, 127–141.
[38] Studer H. Antimicrobial protection for polyolefin fibers. *Chem. Fibers Int.* 1997, 47, 373–374.
[39] Dev VRG, Venugopal J, Sudha S, Deepika G, Ramakrishna S. Dyeing and antimicrobial characteristics of chitosan treated wool fabrics with henna dye. *Carbohydr. Polym.* 2009, 75, 646–650.
[40] Bobbarala V, Ed., *Antimicrobial Agents*, InTech: Rijeka, Croatia, 2012.
[41] Lee HJ, Yeo SY, Jeong SH. Antibacterial effect of nanosized silver colloidal solution on textile fabrics. *J. Mater. Sci.* 2003, 38, 2199.
[42] Trotman ER, *Dyeing and Chemical Technology of Textile Fibres*. John Wiley & Sons Inc.: NY, 1984.
[43] Anita S, Ramachandran T, Rajendran R, Koushik CV, Mahalakshmi M. A study of the antimicrobial property of encapsulated copper oxide nanoparticles on cotton fabric. *Text. Res. J.* 2011, 81, 1081–1088.
[44] Kathirvelu S, D'Souza L, Dhurai B. UV protection finishing of textiles using ZnO nanoparticles. *Indian J. Fibre Text. Res.* 2009, 34, 267–273.
[45] Gupta B, Agarwal R, Alam MS. Textile-based smart wound dressings, *Indian J. Fibre Text. Res.* 2010, 35, 174–187.
[46] Borsuk DE, Gallant M, Richard D, Williams HB. Silver-coated nylon dressings for pediatric burn victims. *Can. J. Plast. Surg.* 2007, 15, 29–31.
[47] Chen X, Schluesener HJ. Nanosilver: a nanoproduct in medical application, *Toxicol. Lett.* 2008, 176, 1–12.
[48] Jo YK, Kim BH, Jung G. Antifungal activity of silver ions and nanoparticles on phytopathogenic fungi. *Plant. Dis.* 2009, 93, 1037–1043.
[49] Dunn K, Edwards-Jones V. The role of Acticoat with nanocrystalline silver in the management of burns. *Burns* 2004, 30, 1–9.
[50] Chopra I. The increasing use of silver-based products as antimicrobial agents: a useful development or a cause for concern? *J. Antimicrob. Chemother.* 2007, 60, 447–448.
[51] Wright T. Alphasan a thermally stable silver-based inorganic antimicrobial technology. *Chem. Fibers Int.* 2002, 25, 125.
[52] Kim JS, Kuk E, Yu KN, Kim JH, Park SJ, Lee HJ, Kim SH, Park YK, Park YH, Hwang CY, Kim YK, Lee YS, Jeong DH, Cho MH. Antimicrobial effects of silver nanoparticles. *Nanomed.: Nanotechnol. Biol. Med.* 2007, 3, 95–101.
[53] Kaur P, Saxena M, Vadehra DV. Plasmid mediated resistance to silver ions in *Escherichia coli*. *Indian J. Med. Res.* 1985, 82, 122–126.
[54] Kumar VS, Nagaraja BM, Shashikala V, Padmasri AH, Madhavendra SS, Raju BD, Rama Rao KS. Highly efficient Ag/C catalyst prepared by electro-chemical deposition method in controlling microorganisms in water. *J. Mol. Catal. A: Chem.* 2004, 223, 313–319.

[55] Sathishkumar M, Sneha K, Won SW, Cho CW, Kim S, Yun YS. *Cinnamon zeylanicum* bark extract and powder mediated green synthesis of nanocrystalline silver particles and its bactericidal activity. *Colloids Surf. B.* 2009, 73, 332–338.
[56] Rusell AD, Hugo WB. Antimicrobial activity and action of silver. *Prog. Med. Chem.* 1994, 31, 351–370.
[57] Rosenkranz HS, Carr HS. Silver sulfadiazine: effect on the growth and metabolism of bacteria. *J. Antimicrob. Chemother.* 1972, 2, 367–372.
[58] Goddard PA, Bull AT. Accumulation of silver by growing and nongrowing population of *Citrobacter intermedius* B5. *Appl. Microbiol. Biotechnol.* 1989, 31, 314–319.
[59] Percival SL, Bowler PG, Russell D. Bacterial resistance to silver in wound care. *J. Hosp. Infect.* 2005, 60, 1–7.
[60] Percival SL, Thomas J, Linton S, Okel T, Corum L, Slone W. The antimicrobial efficacy of silver on antibiotic-resistant bacteria isolated from burn wounds. *Int. Wound J.* 2012, 9, 488–493.
[61] Brogliato AR, Borges PA, Barros JF, Lanzetti M, Valenca S, Oliveira NC, JIzario-Filho H, Benjamim CF. The effect and safety of dressing composed by nylon threads covered with metallic silver in wound treatment. *Int. Wound J.* 2012. doi: 10.1111/j.1742-481X.2012.01065.x [ahead of print].
[62] Lorenz C, Windler L, von Goetz N, Lehmann RP, Schuppler M, Hungerbuhler K, Heuberger M, Nowack B. Characterization of silver release from commercially available functional (nano) textile. *Chemosphere* 2012, 89, 817–824.
[63] Lok CN, Ho CM, Chen R, He QY, Yu WY, Sun H, Tam PKH, Chiu JF, Che CM. Proteomic analysis of the mode of antibacterial action of silver nanoparticles. *J. Proteome Res.* 2006, 5, 916–924.
[64] Nair S, Laurencin CT. Silver nanoparticles: synthesis and therapeutic applications. *J. Biomed. Nanotechnol.* 2007, 3, 301–316.
[65] Chappel JB, Greville GD. Effect of silver ions on mitochondrial adenosine triphosphatase. *Nature.* 1954, 174, 930–931.
[66] Cecil R, McPhee JR. The sulfur chemistry of proteins. In *Advances in Protein Chemistry,* Anfinsen, CB, Ed., Academic Press Inc.: New York, 1959, pp. 255–389.
[67] Rogers KS. Variable sulfhydryl activity toward silver nitrate by reduced glutathione and alcohol, glutamate and lactate dehydrogenase. *Biochim. Biophys. Acta.* 1972, 263, 309–314.
[68] Foster TJ. Plasmid-determined resistance to antimicrobial drugs and toxic metal ions in bacteria. *Microbiol. Rev.* 1983, 47, 361–409.
[69] Rayman ML, Lo TCY, Sanwal BD. Transport of succinate in *Escherichia coli*. II. Caracteristics of uptake and energy coupling with transport in membrane preparations. *J. Biol. Chem.* 1972, 247, 6332–6339.
[70] Shaw WHR. The inhibition of urease by various metal ions. *J. Am. Chem. Soc.* 1954, 76, 2160–2163.
[71] Feng QL, Wu J, Chen GQ, Cui FZ, Kim TN, Kim JO. A mechanistic study of the antibacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*. *J. Biomed. Mater. Res.* 2000, 52, 662–668.
[72] Yang W, Shen C, Ji Q, An H, Wang J, Liu Q, Zhang Z. Food storage material silver nanoparticles interfere with DNA replication fidelity and bind with DNA. *Nanotechnology* 2009, 20, 085102.
[73] Park HJ, Kim JY, Kim J, Lee JH, Hahn JS, Gu MB, Yoon J. Silver-ion-mediated reactive oxygen species generation affecting bactericidal activity. *Water Res.* 2009, 43, 1027–1032.
[74] Holt KB, Bard AJ. The interaction of silver (I) ions with the respiratory chain of *Escherichia coli*: an electrochemical and scanning electrochemical microscopy study of the antimicrobial mechanism of micromolar Ag^+. *Biochemistry* 2005, 44, 13214–13223.
[75] Morones JR, Elechiguerra JL, Camacho A, Holt K, Kouri JB, Ramírez JT, Yacaman MJ. The bactericidal effect of silver nanoparticles. *Nanotechnology* 2005, 16, 2346.
[76] Raffi M, Hussain F, Bhatti TM, Akhter JI, Hameed A, Hasan MM. Antibacterial characterization of silver nanoparticles against *E. coli* ATCC-15224. *J. Mater. Sci. Technol.* 2008, 24, 192–196.
[77] Hwang ET, Lee JH, Chae YJ, Kim YS, Kim BC, Sang BI, Gu MB. Analysis of the toxic mode of action of silver nanoparticles using stress-specific bioluminescent bacteria. *Small* 2008, 4, 746–750.
[78] Amro NA, Kotra LP, Wadu-Mesthrige K, Bulychev A, Mobashery S, Liu GY. High-resolution atomic force microscopy studies of the *Escherichia coli* outer membrane: structural basis for permeability. *Langmuir* 2000, 16, 2789–2796.
[79] Sondi I, Salopek-Sondi B. Silver nanoparticles as antimicrobial agent: a case study on *E. coli* as a model for Gram-negative bacteria. *J. Colloid Interface Sci.* 2004, 275, 177–182.
[80] Faundez G, Troncoso M, Navarrete P, Figuero G. Antimicrobial activity of copper surfaces against suspensions of *Salmonella enterica* and *Campylobacter jejuni*. *BMC Microbiol.* 2004, 4, 19.
[81] Mary G, Bajpai SK, Chand N. Copper alginate-cotton cellulose (CACC) fibers with excellent antibacterial properties. *J. Eng. Fiber. Fabr.* 2009, 4, 24–35.
[82] Dollwet HHA, Sorenson JRJ. Historic uses of copper compounds in medicine. *Trace Elem. Med.* 1985, 2, 80–87.
[83] Sorenson JRJ. Copper chelates as possible active forms of the antiarthritic agents. *J. Med. Chem.* 1976, 19, 135–148.
[84] Sorenson JRJ. Some copper coordination compounds and their anti-inflammatory and antiulcer activities. *Inflammation* 1976, 1, 317–331.
[85] Borkow G, Gabbay J. Copper as a biocidal tool. *Curr. Med. Chem.* 2005, 12, 2163–2175.
[86] Borkow G, Gabbay J. Putting copper into action: copper-impregnated products with potent biocidal activities. *FASEB J.* 2004, 18, 1728–1730.
[87] Peña MMO, Koch KA, Thiele DJ. Dynamic regulation of copper uptake and detoxification genes in *Saccharomyces cerevisiae*. *Mol. Cell. Biol.* 1998, 18, 2514–2523.
[88] Cervantes C, Gutierrez-Corona F. Copper resistance mechanisms in bacteria and fungi. *FEMS Microbiol. Rev.* 1994, 14, 121–137.
[89] Ohsumi Y, Kitamoto K, Anraku YJ. Changes induced in the permeability barrier of the yeast plasma membrane by cupric ion. *J. Bacteriol.* 1988, 170, 2676–2682.
[90] Stohs SJ, Bagchi D. Oxidative mechanisms in the toxicity of metal ions. *Free Radic. Biol. Med.* 1995, 18, 321–336.
[91] Blackett PR, Lee DM, Donaldson DL, Fesmire JD, Chan WY, Holcombe JH, Rennert OM. Studies of lipids, lipoproteins, and apolipoproteins in Menkes' disease. *Pediatr. Res.* 1984, 18, 864–870.
[92] Ding AH, Chan PC. Singlet oxygen in copper-catalyzed lipid peroxidation in erythrocyte membranes. *Lipids.* 1984, 19, 278–284.
[93] Chan PC, Peller OG, Kesner L. Copper(II)-catalyzed lipid peroxidation in liposomes and erythrocyte membranes. *Lipids* 1982, 17, 331–337.

[94] Winge DR, Jensen LT, Srinivasan C. Metal-ion regulation of gene expression in yeast. *Curr. Op. Chem. Biol.* 1998, 2, 216–221.
[95] Eide DJ. The molecular biology of metal ion transport in *Saccharomyces cerevisiae*. *Annu. Rev.* 1998, 18, 441–469.
[96] Hasset R, Kosman DJ. Evidence for Cu(II) reduction as a component of copper uptake by *Saccharomyces cerevisiae*. *J. Biol. Chem.* 1995, 270, 128–134.
[97] Georgatsou E, Mavrogiananis LA, Fragiadakis GS, Alexandrak D. The yeast Fre1p/Fre2p cupric reductases facilitate copper uptake and are regulated by the copper-modulated Mac1p activator. *J. Biol. Chem.* 1997, 272, 13786–13792.
[98] Labbe S, Zhu Z, Thiele DJ. Copper-specific transcriptional repression of yeast genes encoding critical components in the copper transport pathway. *J. Biol. Chem.* 1997, 272, 15951–15958.
[99] Yamaguchi-Iwai Y, Serpe M, Haile D, Kosman DJ, Yang W, Klausner DJ, Dancis A. Homeostatic regulation of copper uptake in yeast via direct binding of MAC1 protein to upstream regulatory sequences of FRE1 and CTR1. *J. Biol. Chem.* 1997, 272, 17711–17718.
[100] Jungmann J, Reins HA, Lee J, Romeo A, Hasset R, Kosman D, Jentsch S. MAC1, a nuclear regulatory protein related to Cu-dependent transcription factors is involved in Cu/Fe utilization and stress resistance in yeast. *EMBO J.* 1993, 12, 5051–5056.
[101] Fürst P, Hu S, Hackett R, Hamer D. Copper activates metallothionein gene transcription by altering the conformation of a specific DNA binding protein. *Cell* 1988, 55, 705–717.
[102] Thiele DJ. ACE1 regulates expression of the *Saccharomyces cerevisiae* metallothionein gene, *Mol. Cell. Biol.* 1988, 8, 2745–2752.
[103] Zhou P, Thiele DJ. Copper and gene regulation in yeast. *Biofactors*. 1993, 4, 105–115.
[104] Lin SJ, Culotta VC. The ATX1 gene of *Saccharomyces cerevisiae* encodes a small metal homeostasis factor that protects cells against reactive oxygen toxicity. *Proc. Natl. Acad. Sci. USA* 1995, 92, 3784–3788.
[105] Lin SJ, Pufahl RA, Dancis A, O'Halloran TV, Culotta VC. A role for the *Saccharomyces cerevisiae* ATX1 gene in copper trafficking and iron transport. *J. Biol. Chem*. 1997, 272, 9215–9220.
[106] Glerum DM, Shtanko A, Tzagoloff A. Characterization of COX17, a yeast gene involved in copper metabolism and assembly of cytochrome oxidase. *J. Biol. Chem.* 1996, 271, 14504–14509.
[107] Culotta VC, Klomp LW, Strain J, Casareno RL, Krems B, Gitlin JD. The copper chaperone for superoxide dismutase. *J. Biol. Chem.* 1997, 272, 23469–23472.
[108] Craddock PT. *2000 Years of Zinc and Brass*. British Museum Press: London, 1998.
[109] Craddock PT. Mining and metallurgy. In *The Oxford Handbook of Engineering and Technology in the Classical World,* Oleson, JP, Eds. London: Oxford University Press, 2008, pp. 111–112.
[110] El Shafei A, Shaarawy S, Hebeish A. Application of reactive cyclodextrin poly butyl acrylate preformed polymers containing nano-ZnO to cotton fabrics and their impact on fabric performance. *Carbohydr. Polym.* 2010, 79, 852–857.
[111] Sawai J, Igarashi H, Hashimoto A, Kokugan T, Shimizu M. Effect of particle size and heating temperature of ceramic powders on antibacterial activity of their slurries. *J. Chem. Eng. Jpn.* 1996, 29, 251–256.
[112] Sawai J, Kawada E, Kanou F, Igarashi H, Hashimoto A, Kokugan T, Shimizu M. Detection of active oxygen generated from ceramic powders having antibacterial activity. *J. Chem. Eng. Jpn.* 1996, 29, 627–633.
[113] Applerot G, Lipovsky A, Dror R, Perkas N, Nitzan Y, Lubart R, Gedanken A. Enhanced antibacterial activity of nanocrystalline ZnO due to increased ROS mediated cell injury. *Adv. Funct. Mater.* 2009, 19, 842–852.
[114] Huang Z, Zheng X, Yan D, Yin G, Liao X, Kang Y, Yao Y, Huang D, Hao B. Toxicological effect of ZnO nanoparticles based on bacteria. *Langmuir* 2008, 24, 4140–4144.
[115] Nair S, Sasidharan A, Divya Rani VV, Menon D, Nair S, Manzoor K. Role of size scale of ZnO nanoparticles and microparticles on toxicity toward bacteria and osteoblast cancer cells. *J. Mater. Sci.: Mater. Med.* 2009, 20, 235–241.
[116] Sawai J, Igarashi H, Hashimoto A, Kokugan T, Shimizu M. Evaluation of growth inhibitory effect of ceramics powder slurry on bacteria by conductance method. *J. Chem. Eng. Jpn.* 1995, 28, 288–293.
[117] Sawai J, Saito I, Kanou F, Igarashi H, Hashimoto A, Kokugan T, Shimizu M. Mutagenicity test of ceramic powder which have growth inhibitory effect on bacteria. *J. Chem. Eng. Jpn.* 1995, 28, 352–354.
[118] Sawai J, Kojima H, Igarashi H, Hashimoto A, Shoji S, Takehara A, Sawaki T, Kokugan T, Shimizu M. *Escherichia coli* damage by ceramic powder slurries. *J. Chem. Eng. Jpn.* 1997, 30, 1034–1039.
[119] Sawai J, Shoji S, Igarashi H, Hashimoto A, Kokugan T, Shimizu M, Kojima H. Hydrogen peroxide as an antibacterial factor in zinc oxide powder slurry. *J. Ferment. Bioeng.* 1998, 86, 521–522.
[120] Yang ZH, Xie CS. Zn^{2+} release from zinc and zinc oxide particles in simulated uterine solution. *Colloids Surf. B.* 2006, 47, 140–145.
[121] Zhang L, Jiang Y, Ding Y, Povey M, York D. Investigation into the antibacterial behaviour of suspensions of ZnO nanoparticles (ZnO nanofluids). *J. Nanopart. Res.* 2007, 9, 479–489.
[122] Brayner R, Ferrari-Iliou R, Brivois N, Djediat S, Benedetti MF, Fiévet F. Toxicological impact studies based on *Escherichia coli* bacteria in ultrafine ZnO nanoparticles colloidal medium. *Nano Lett.* 2006, 6, 866–870.
[123] Windler L, Height M, Nowack B. Comparative evaluation of antimicrobials for textile applications. *Environ. Int.* 2013, 53, 62–73.
[124] Grancaric AM, Rybicki E, Tarbuk A, Pavlovic G, Botteri L. Nanoparticles of silver in antimicrobial treatment of textiles. *Textile* 2012, 60, 629–639.
[125] Panácek A, Kolár M, Vecerová R, Prucek R, Soukupová J, Krystof V, Hamal P, Zboril R, Kvítek L. Antifungal activity of silver nanoparticles against *Candida* spp. *Biomaterials* 2009, 30, 6333–6340.
[126] Elechiguerra JL, Burt JL, Morones JR, Camacho-Bragado A, Gao X, Lara HH, Yacaman MJ. Interaction of silver nanoparticles with HIV-1. *J. Nanobiotechnology* 2005, 3, 6.
[127] Lu L, Sun RW, Chen R, Hui CK, Ho CM, Luk JM, Lau GK, Che CM. Silver nanoparticles inhibit hepatitis B virus replication. *Antivir. Ther.* 2008, 13, 253–262.

[128] Lara HH, Ayala-Nuñez NV, Ixtepen-Turrent L, Rodriguez-Padilla C. Mode of antiviral action of silver nanoparticles against HIV 1. *J. Nanobiotechnol.* 2010, 8, 1.
[129] Lara HH, Ayala-Nuñez NV, Ixtepen-Turrent L, Rodriguez-Padilla C. Bactericidal effect of silver nanoparticles against multidrug-resistant bacteria. *World J. Microb. Biotechnol.* 2010, 26, 615–621.
[130] Sambhy V, MacBride MM, Peterson BR, Sen A. Silver bromide nanoparticle/polymer composites: dual action tunable antimicrobial materials. *J. Am. Chem. Soc.* 2006, 128, 9798–9808.
[131] Ricci G, Patrizi A, Mandrioli P, Specchia F, Medri M, Menna G, Masi M. Evaluation of the antibacterial activity of a special silk textile in the treatment of atopic dermatitis. *Dermatology* 2006, 213, 224–227.
[132] Daeschlein G, Assadian O, Arnold A, Haase H, Kramer A, Jünger M. Bacterial burden of worn therapeutic silver textiles for neurodermitis patients and evaluation of efficacy of washing skin. *Pharmacol. Physiol.* 2010, 23, 86–90.
[133] Gauger A, Fisher S, Mempel M, Schaefer T, Foelster-Holst R, Abeck D, Ring J. Efficacy and functionality of silver-coated textiles in patients with atopic eczema. *Eur. Acad. Dermatol. Venereol.* 2006, 20, 534–541.
[134] Rai M, Yadav A, Gade A. Silver nanoparticles as a new generation of antimicrobials. *Biotechnol. Adv.* 2009, 27, 76–83.
[135] Jain P, Pradeep T. Potential of silver nanoparticle-coated polyurethane foam as an antibacterial water filter. *Bioechnol. Bioeng.* 2005, 90, 59–63.
[136] Gittard SD, Hojo D, Hyde GK, Scarel G, Narayan RJ, Parsons GN. Antifungal textiles formed using silver deposition in supercritical carbon dioxide. *J. Mater. Eng. Perform.* 2010, 19, 368–373.
[137] Babu KF, Dhandapani P, Maruthamuthu S, Kulandainathan MA. One pot synthesis of polypyrrole silver nanocomposite on cotton fabrics for multifunctional property. *Carbohydr. Polym.* 2012, 90, 1557–1563.
[138] Gupta P, Bajpai M, Bajpai SK. Investigation of antibacterial properties of silver nanoparticle-loaded poly(acrylamide-co-itaconic-acid)-grafted cotton fabric. *J. Cotton Sci.* 2008, 12, 280–286.
[139] Tomšič B, Simončič B, Orel B, Černe L, Tavčer PF, Zorko M, Jerman I, Vilčnik A, Kovač J. Sol-gel coating of cellulose fibres with antimicrobial and repellent properties. *J. Sol-Gel Sci. Technol.* 2008, 47, 44–57.
[140] Gouda M. Nano-zirconium oxide and nano-silver oxide/cotton gauze fabrics for antimicrobial and wound healing acceleration. *J. Ind. Text.* 2012, 41, 222–240.
[141] Chmielewska D, Sartowska B. Radiation synthesis of silver nanostructures in cotton matrix. *J. Mater. Sci.* 2012, 47. 5721–5728.
[142] Nourbakhsh S, Ashjaran A. Laser treatment of cotton fabric for durable antibacterial properties of silver nanoparticles. *Materials* 2012, 5, 1247–1257.
[143] Tomšič B, Simončič B, Orel B, Žerjav M, Schroers H, Simončič A, Samardžija Z. Antimicrobial activity of AgCl embedded in a silica matrix on cotton fabric. *Carbohydr. Polym.* 2009, 75, 618–626.
[144] Tomšič B, Klemenčič D, Simončič B, Orel B. Influence of antimicrobial finishes on the biodeterioration of cotton and cotton/polyester fabrics: leaching versus bio-barrier formation. *Polym. Degrad. Stabil.* 2011, 96, 1286–1296.
[145] Tang B, Wang JF, Xu SP, Afrin T, Tao JL, Xu WQ, Sun L, Wang XG. Function improvement of wool fabric based on surface assembly of silica and silver nanoparticles. *Chem. Eng. J.* 2012, 185, 366–373.
[146] Potiyaraj P, Kumlangdudsana P, Dubas ST. Synthesis of silver chloride nanocrystal on silk fibers. *Mater. Lett.* 2007, 61, 2464–2466.
[147] Wang S, Hou W, Wei L, Jia H, Liu X, Xu B. Antibacterial activity of nano-SiO_2 antibacterial agent grafted on wool surface. *Surf. Coat. Technol.* 2007, 202, 460–465.
[148] Ki HY, Kim JH, Kwon SC, Jeong SH. A study on multifunctional wool textiles treated with nano-sized silver. *J. Mater. Sci.* 2007, 42, 8020–8024.
[149] Park SY, Chung JW, Priestley RD, Kwak SY. Covalent assembly of metal nanoparticles on cellulose fabric and its antimicrobial activity. *Cellulose* 2012, 19, 2141–2151.
[150] Parikh DV, Fink T, Rajasekharan K, Sachinvala ND, Sawhney APS, Calamari TA, Parikh AD. Antimicrobial silver/sodium carboxymethyl cotton dressings for burn wounds. *Text Res. J.* 2005, 75, 134–138.
[151] Nischala K, Rao TN, Hebalkar N. Silica-silver core-shell particles for antibacterial textile application. *Colloids Surf. B.* 2011, 82, 203–208.
[152] Hadad L, Perkas N, Gofer Y, Calderon-Moreno J, Ghule A, Gedanken A. Sonochemical deposition of silver nanoparticles on wool fibers. *J. Appl. Polym. Sci.* 2007, 3, 1732–1737.
[153] Kim SS, Park JE, Lee J. Properties and antimicrobial efficacy of cellulose fiber coated with silver nanoparticles and 3-mercaptopropyltrimethoxysilane (3-MPTMS). *J. Appl. Polym. Sci.* 2011, 119, 2261–2267.
[154] Hebeish A, El-Shafei A, Sharaf S, Zaghloul S. Novel precursors from green synthesis and application of silver nanoparticles in the realm of cotton finishing. *Carbohydr. Polym.* 2011, 84, 605–613.
[155] Hebeish A, El-Naggar ME, Fouda MMG, Ramadan MA, Al-Deyab SS, El-Rafie MH. Highly effective antibacterial textiles containing green synthesized silver nanoparticles. *Carbohydr. Polym.* 2011, 86, 936–940.
[156] Tang B, Wang J, Xu S, Afrin T, Xu W, Sun L, Wang X. Application of anisotropic silver nanoparticles: multifunctionalization of wool fabric. *J. Colloidal Interface Sci.* 2011, 356, 513–518.
[157] Kelly FM, Johnston JH. Colored and functional silver nanoparticle-wool fiber composites. *Appl. Mater. Interfaces* 2011, 3, 1083–1092.
[158] Rad PS, Montazer M, Rahimi MK. Simultaneous antimicrobial and dyeing of wool: a facial method. *J. Appl. Polym. Sci.* 2011, 1 22, 1405–1411.
[159] Gorenšek M, Recelj P. Nanosilver functionalized cotton fabric. *Text Res. J.* 2007, 77, 138–141.
[160] Hosseinkhani M, Montazer M, Eskandarnejad S, Rahimi MK. Simultaneous *in situ* synthesis of nano silver and wool fiber fineness enhancement using sulphur based reducing agents. *Colloids Surf. A.* 2012. 415. 431–438.
[161] Pollini M, Paladini F, Licciulli A, Maffezzoli A, Nicolais L, Sannino A. Silver coated wool yarns with durable antibacterial properties. *J. Appl. Polym Sci.* 2012, 125, 2239–2244.
[162] El-Rafie MH, Mohamed AA, Shaheen TI, Hebeish A. Antimicrobial effect of silver nanoarticles produced by fungal process on cotton fabrics. *Carbohydr. Polym.* 2010, 80, 779–782.

[163] Ravindra S, Mohan YM, Reddy NN, Raju KM. Fabrication of antibacterial cotton fibres loaded with silver nanoparticles via "Green Approach". *Colloids Surf. A.* 2010, 367, 31–40.
[164] El-Shishtawy RM, Asiri AM, Abdelwahed NAM, Al-Otaibi MM. *In situ* production of silver nanoparticle on cotton fabric and its antimicrobial evaluation. *Cellulose* 2011, 18, 75–82.
[165] Thomas V, Bajpai M, Bajpai SK. *In situ* formation of silver nanoparticles within chitosan-attached cotton fabric for antibacterial property. *J. Ind. Text.* 2011, 40, 229–245.
[166] Durán N, Marcato PD, De Souza GIH, Alves OL, Esposito E. Antibacterial effect of silver nanoparticles produced by fungal process on textile fabrics and their effluent treatment. *J. Biomed. Nanotechnol.* 2007, 3, 203–208.
[167] Falletta E, Bonini M, Fratini E, Lo Nostro A, Pesavento G, Becheri A, Lo Nostro P, Canton P, Baglioni P. Clusters of poly(acrylates) and silver nanoparticles: structures and applications for antimicrobial fabrics. *J. Phys. Chem. C.* 2008, 112, 11758–11766.
[168] Hegemann D, Hossain MM, Balazs DJ. Nanostructured plasma coatings to obtain multifunctional textile surfaces. *Progr. Org. Coat.* 2007, 58, 237–240.
[169] Khoddami A, Shokohi SS, Morshed M, Abedi D. Simultaneous application of silver nanoparticles with different crease resistant finishes. *Fibers Polym.* 2011, 12, 635–641.
[170] Abdel-Mohsen AM, Abdel-Rahman RM, Hrdina R, Imramovsky A, Burgert L, Aly AS. Antibacterial cotton fabrics treated with core-shell nanoparticles. *Int. J. Biol. Macromol.* 2012, 50, 1245–1253.
[171] Ureyen ME, Dogan A, Koparal AS. Antibacterial functionalization of cotton and polyester fabrics with a finishing agent based on silver-doped calcium phosphate powders. *Text. Res. J.* 2012, 82, 1731–1742.
[172] Mejía MI, Restrepo G, Marín JM, Sanjines R, Pulgarín C, Mielczarski E, Mielczarski J, Kiwi J. Magnetron-sputtered Ag surfaces. New evidence for the nature of the Ag ions intervening in bacterial inactivation. *ACS Appl. Mater. Int.* 2010, 1, 230–235.
[173] Abbasi AR, Bohloulzadeh M, Morsali A. Preparation of AgCl nanoparticles@ancient textile with antibacterial activity under ultrasound irradiation. *J. Inorg. Organomet. Polym.* 2011, 21, 504–510.
[174] Khalil-Abad MS, Yazdanshenas ME. Superhydrophobic antibacterial cotton textiles. *J. Colloidal Interface Sci.* 2010, 351, 293–298.
[175] Xue CH, Chen J, Yin W, Jia ST, Ma JZ. Superhydrophobic conductive textiles with antibacterial property by coating fibers with silver nanoparticles. *Appl. Surf. Sci.* 2012, 58, 2468–2472.
[176] Shastri JP, Rupani MG, Jain RL. Antimicrobial activity of nanosilver-coated socks fabrics against foot pathogens. *J. Text. Inst.* 2012, 103, 1234–1243.
[177] Kostić M, Radić N, Obradović BM, Dimitrijević S, Kuraica MM, Škundrić P. Silver loaded cotton/polyester fabric modified by dielectric barrier discharge treatment. *Plasma Process. Polym.* 2009, 6, 58–67.
[178] Dubas ST, Kumlangdudsana P, Potiyaraj P. Layer-by-layer deposition of antimicrobial silver nanoparticles on textile fibres. *Colloids Surf. A.* 2006, 289, 105–109.
[179] Xu H, Shi X, Lv YH, Mao ZP. The preparation and antibacterial activity of polyester fabric loaded with silver nanoparticles. *Text. Res. J.* 2013, 83, 321–326.
[180] Mahltig B, Textor T. Silver containing sol-gel coatings on polyamide fabrics as antimicrobial finish-description of a technical application process for wash permanent antimicrobial effect. *Fibres Polym.* 2010, 11, 1152–1158.
[181] Mahltig B, Fischer A. Inorganic/organic polymer coatings for textiles to realize water repellent and antimicrobial properties – a study with respect to textile comfort. *J. Polym. Sci.: Part B: Polym. Phys.* 2010, 48, 1562–1568.
[182] MacKeen PC, Person S, Warner SC, Snipes W, Stevens Jr SE. Silver coated nylon fibre as an antibacterial agent. *Antimicrob. Agents Chemother.* 1987, 31, 93–99.
[183] Deitch EA, Marino AA, Gillespie TE, Albright JA. Silver nylon: a new antimicrobial agent. *Antimicrob. Agents Chemother.* 1983, 23, 356–359.
[184] Jiang SX, Qin WF, Guo RH, Zhang L. Surface functionalization of nanostructured silver-coated polyester fabric by magnetron sputtering. *Surf. Coat. Technol.* 2010, 204, 3662–3667.
[185] Jiang SX, Qin WF, Tao XM, Zhang ZM, Yuen CWM, Xiong J, Kan CW, Zhang L, Guo RH, Shang SM. Surface characterization of sputter silver-coated polyester fiber. *Fibers Polym.* 2011, 12, 616–619.
[186] Azadbakht A, Abbasi AR. Synthesis and characterization of acrylic fibers with antibacterial silver nanoparticles. *Fibers Polym.* 2012, 13, 264–268.
[187] Ilić V, Šaponjić Z, Vodnik V, Potkonjak B, Jovančić P, Nedeljković J. The influence of silver content on antimicrobial activity and color of cotton fabrics functionalized with Ag nanoparticles. *Carbohydr. Polym.* 2009, 78, 564–569.
[188] Shi Q, Vitchuli N, Nowak J, Caldwell JM, Breidt F, Bourham M, Zhang X, McCord M. Durable antibacterial Ag/polyacrylonitrile (Ag/PAN) hybrid nanofibers prepared by atmospheric treatment and electrospinning. *Eur. Polym. J.* 2011, 47, 1402–1409.
[189] Rivero PJ, Urrutia A, Goicoechea J, Rodríguez Y, Corres JM, Arregui FJ, Matías IR. An antibacterial submicron fiber mat with in situ synthesized silver nanoparticles. *J. Appl. Polym. Sci.* 2012, 126, 1228–1235.
[190] Gawish SM, Avci H, Ramadan AM, Mosleh S, Monticello R, Breidt F, Kotek R. Properties of antibacterial polypropylene/nanometal composite fibers. *J. Biomater. Sci.* 2012, 23, 43–61.
[191] Khajavi R, Bahadoran MMS, Bahador A, Khosravi A. Removal of microbes and air pollutants passing through nonwoven polypropylene filters by activated carbon and nanosilver colloidal layers. *J. Ind. Text.* 2013, 42, 219–230.
[192] Baghriche O, Ruales C, Sanjines R, Pulgarin C, Zertal A, Stolitchnov I, Kiwi J. Ag-surfaces sputtered by DC and pulsed DC-magnetron sputtering effective in bacterial inactivation: testing and characterization. *Surf. Coat. Technol.* 2012, 206, 2410–2416.
[193] Cioffi N, Ditaranto N, Torsi L, Sabbatini L. Approaches to synthesis and characterization of spherical and anisotropic copper nanomaterials. In *Nanomaterials for the Life Sciences, Metallic Nanomaterials*, Kumar, C, Ed., Wiley-VCH: Weinheim, 2009, pp. 3–70.
[194] Cioffi N, Ditaranto N, Torsi L, Picca RA, De Giglio E, Sabbatini L, Novello L, Tantillo G, Bleve-Zacheo T, Zambonin PG. Synthesis, analytical characterization and bioactivity of Ag and Cu nanoparticles embedded in poly-vinyl-methyl-ketone films. *Anal. Bioanal. Chem.* 2005, 382, 1912–1918.

[195] Tyrone LV, Benjaminson MA. Antibacterial fiber treatments and disinfection. *Text. Res. Inst.* 1981, 454–465.
[196] Torres A, Ruales C, Pulgarin C, Aimable A, Bowen P, Sarria V, Kiwi J. Innovative high-surface-area CuO pretreated cotton effective in bacterial inactivation under visible light. *ACS Appl. Mater. Interfaces* 2010, 2, 2547–2552.
[197] Castro C, Sanjines R, Pulgarin C, Osorio P, Giraldo SA, Kiwi J. Structure-reactivity relations for DC-magnetron sputtered Culayers during *E. coli* inactivation in the dark and under light. *J. Photochem. Photobiol. A.* 2010, 216, 295–302.
[198] Osorio-Vargas P, Sanjines R, Ruales C, Castro C, Pulgarin C, Rengifo-Herrera AJ, Lavanchy JC, Kiwi J. Antimicrobial Cu-functionalized surfaces prepared by bipolar asymmetric DC-pulsed magnetron sputtering (DCP). *J. Photochem. Photobiol. A.* 2011, 220, 70–76.
[199] Perelshtein I, Applerot G, Perkas N, Wehrschuetz-Sigl E, Hasmann A, Guebitz G, Gedanken A. CuO-cotton nanocomposite: formation, morphology, and antibacterial activity. *Surf. Coat. Technol.* 2009, 204, 54–57.
[200] Abramov OV, Gedanken A, Koltypin Y, Perkas N, Perelshtein I, Joyce E, Mason TJ. Pilot scale sonochemical coating of nanoparticles onto textiles to produce biocidal fabrics. *Surf. Coat. Technol.* 2009, 204, 718–722.
[201] Chattopadhyay DP, Patel BH. Effect of nanosized colloidal copper on cotton fabric. *J. Eng. Fiber Fabr.* 2010, 5, 1–6.
[202] Grace M, Chand N, Sunil KB. Copper alginate-cotton cellulose (CACC) fibers with excellent antibacterial properties. *J. Eng. Fiber Fabr.* 2009, 4, 24–35.
[203] Grace M, Bajpai SK, Chand N. Copper (II) ions and copper nanoparticles-loaded chemically modified cotton cellulose fibers with fair antibacterial properties. *J. Appl. Polym. Sci.* 2009, 11, 757–766.
[204] Berendjchi A, Khajavi R, Yazdanshenas MS. Fabrication of superhydrophobic and antibacterial surface on cotton fabric by doped silica-based sols with nanoparticles of copper. *Nanoscale Res. Lett.* 2011, 6, 594–602.
[205] Gabbay J, Borkow G, Mishal J, Magen E, Zatcoff R, Shemer-Avni Y. Copper oxide impregnated textiles with potent biocidal activities. *J. Ind. Text.* 2006, 35, 323–335.
[206] Ehiasarian A, Pulgarin C, Kiwi J. Inactivation of bacteria under visible light and in the dark by Cu films. Advantages of Cu-HIPIMS-sputtered films. *Environ. Sci. Pollut. Res.* 2012, 19, 3791–3797.
[207] Rio L, Kusiak-Nejman E, Kiwi, Betrisey B, Pulgarin C, Trampuz A, Bizzini A. Comparison of methods for evaluation of the bactericidal activity of copper-sputtered surfaces against methicillin-resistant *Staphylococcus aureus*. *Appl. Environ. Microbiol.* 2012, 78, 8176–8182.
[208] Stoimenov PK, Klinger RL, Marchin GL, Klabunde KJ. Metal oxide nanoparticles as bactericidal agents. *Langmuir* 2002, 18, 6679–6686.
[209] Yadav A, Prasad V, Kathe AA, Raj S, Yadav D, Sundaramoorthy C, Vigneshwaran N. Functional finishing in cotton fabrics using zinc oxide nanoparticles. *Bull. Mater. Sci.* 2006, 29, 641–645.
[210] Vigneshwaran N, Kumar S, Kathe AA, Varadarajan PV, Prasad V. Functional finishing of cotton fabrics using zinc oxide-soluble starch nanocomposites. *Nanotechnology* 2006, 17, 5087–5095.
[211] Becheri A, Dürr M, Lo Nostro P, Baglioni P. Synthesis and characterization of zinc oxide nanoparticles: application to textiles as UV-absorbers. *J. Nanopart. Res.* 2007, 10, 679–689.
[212] Xu T, Xie CS. Tetrapod-like nano-particle ZnO/acrylic resin composite and its multi-function property. *Progr. Org. Coat.* 2003, 46, 297–301.
[213] El Shafei A, Abou-Okeil A. ZnO/carboxymethyl chitosan bionano-composite to impart antibacterial and UV protection for cotton fabric. *Carbohydr. Polym.* 2011, 83, 920–925.
[214] Rajendran R, Balakumar C, Mohammed Ahammed HA, Jayakumar S, Vaideki K, Rajesh EM. Use of zinc oxide nano particles for production of antimicrobial textiles. *Int. J. Eng. Sci. Technol.* 2010, 2, 202–208.
[215] Selvam S, Sundrarajan M. Functionalization of cotton fabric with PVP/ZnO nanoparticles for improved reactive dyeability and antibacterial activity. *Carbohydr. Polym.* 2012, 87, 1419–1424.
[216] Li Q, Chen SL, Jiang WC. Durability of nano ZnO antibacterial cotton fabric to sweat. *J. Appl. Polym. Sci.* 2007, 103, 412–416.
[217] Sivakumar PM, Balaji S, Prabhawathi V, Neelakandan R, Manoharan PT, Doble M. Effective antibacterial adhesive coating on cotton fabric using ZnO nanorods and chalcone. *Carbohydr. Polym.* 2010, 79, 717–723.
[218] Sricharussin W, Threepopnatkul P, Neamjam N. Effect of various shake of zinc oxide nanoparticles on cotton fabric for UV-blocking and anti-bacterial properties. *Fibers Polym.* 2011, 12, 1037–1041.
[219] Subash AA, Chandramouli KV, Ramachandran T, Rajendran R, Muthusamy M. Preparation, characterization, and functional analysis of zinc oxide nanoparticle-coated cotton fabric for antibacterial efficacy. *J. Text. Inst.* 2012, 103, 298–303.
[220] Cakir BA, Budama L, Topel O, Hoda N. Synthesis of ZnO nanoparticles using PS-b-PAA reverse micelle cores for UV protective, self-cleaning and antibacterial textile applications. *Colloids Surf. A: Physicochem. Eng. Aspects* 2012, 414, 132–139.
[221] Iamphaojeen Y, Siriphannon P. Immobilization of zinc oxide nanoparticles on cotton fabrics using poly 4-styrenesulfonic acid polyelectrolyte. *Int. J. Mater. Res.* 2012, 103, 643–647.
[222] Erem AD, Ozcan G, Skrifvars M. Antibacterial activity of PA6/ZnO nanocomposite fibers. *Text Res. J.* 2011, 81, 1638–1646.
[223] Jesionowski T, Kolodziejczak-Radzimska A, Ciesielczyk F, Sífka-Ledakowicz J, Olczyk J, Sielski J. Synthesis of zinc oxide in an emulsion system and its deposition on PES nonwoven fabrics. *Fibres Text.* 2011, 19, 70–75.
[224] Pollini M, Sannino A, Maffezzoli A, Licciulli A. Antibacterial surface treatments based on Silver clusters deposition. EP20050850988 (2008).
[225] Pollini M, Paladini F, Catalano M, Taurino A, Licciulli A, Maffezzoli A, Sannino A. Antibacterial coatings on haemodialysis catheters by photochemical deposition of silver nanoparticles. *J. Mater. Sci. Mater Med.* 2011, 22, 2005–2012.
[226] Pollini M, Paladini F, Licciulli A, Maffezzoli A, Sannino A. Engineering nanostructured silver coatings for antimicrobial applications. In *Nanoantimicrobials Progress and Prospects*, Cioffi, N, Rai, M, Eds., Springer: Heidelberg, Dordrecht, London, and New York. 2012, pp. 313–336.
[227] Pollini M, Russo M, Licciulli A, Sannino A, Maffezzoli A. Characterization of antibacterial silver coated yarns. *J. Mater. Sci. Mater Med.* 2009, 20, 2361–2366.

[228] Wollina U, Heide M, Müller-Litzb W, Obenauf D, Ash J. Functional textiles in prevention of chronic wounds, wound healing and tissue engineering. In *Textiles and the Skin. Current Problems in Dermatology*, Elsener, P, Hatch, K, Wigger-Alberti, W, Eds., Karger Publishers: Basel, 2003, pp. 82–97.
[229] Maneerung T, Tokura S, Rujiravanit R. Impregnation of silver nanoparticles into bacterial cellulose for antimicrobial wound dressing. *Carbohydr. Polym.* 2008, 72, 43–51.
[230] Cioffi N, Ditaranto N, Torsi L, Picca RA, Sabbatini L, Valentini A, Novello L, Novello L, Tantillo G, Bleve-Zacheo T, Zambonin PG. Analytical characterization of bioactive fluoropolymer ultra-thin coatings modified by copper nanoparticles. *Anal. Bioanal. Chem.* 2005, 381, 607–616.
[231] Quaranta F, Valentini A, Rizzi FR, Casamassima G. Dual ion-beam sputter deposition of ZnO films. *J. Appl. Phys.* 1993, 74, 244–248.
[232] Farella I, Valentini A, Cioffi N, Torsi L. Dual ion-beam sputtering deposition of palladium-fluoropolymer nano-composites. *Appl. Phys. A.* 2004, 80, 791–795.
[233] Nitti MA, Valentini A, Senesi GS, Ventruti G, Nappi E, Casamassima G. Ion-beam sputtering deposition of CsI thin films. *Appl. Phys. A.* 2005, 80, 1789–1791.
[234] Reetz MT, Helbig W. Size-selective synthesis of nanostructured transition-metal clusters. *J. Am. Chem. Soc.* 1994, 116, 7401–7402.
[235] Cioffi N, Torsi L, Ditaranto N, Sabbatini L, Zambonin PG. Antifungal activity of polymer-based copper nanocomposite coatings. *Appl. Phys. Lett.* 2004, 85, 2417–2419.
[236] Cioffi N, Torsi L, Ditaranto N, Picca RA, Tantillo G, Sabbatini L, Zambonin PG. Synthesis analytical characterization and bio activity of Ag and Cu containing nano structured membranes. *J. Appl. Biomater. Biomech.* 2004, 2, 200–201.
[237] Cioffi N, Torsi L, Ditaranto N, Tantillo G, Ghibelli L, Sabbatini L, Bleve-Zacheo T, D'Alessio M, Zambonin PG, Traversa E. Copper Nanoparticle/Polymer Composites with Antifungal and Bacteriostatic Properties. *Chem. Mater.* 2005, 17, 5255–5262.
[238] Ditaranto N, Loperfido S, van der Werf I, Mangone A, Cioffi N, Sabbatini L. Synthesis and analytical characterisation of copper-based nanocoatings for bioactive stone artworks treatment. *Anal. Bioanal. Chem.* 2011, 399, 473–481.
[239] Cioffi N, Ditaranto N, Sabbatini L, Torsi L, Zambonin PG. European Patent Application 9 pp Application: EP 2008-EP2123797A1 (2008).
[240] Rai M, Yadav A, Cioffi N. Silver nanoparticles as nano-antimicrobials: bioactivity, benefits and bottlenecks. In *Nanoantimicrobials Progress and Prospects,* Cioffi, N, Rai, M, Eds., Springer: Heidelberg, Dordrecht, London, and New York, 2012, pp. 211–224.
[241] Ivask A, George S, Bodarenko O, Kahru A. Metal-containing nano-antimicrobials: differentiating the impact of solubilized metals and particles. In *Nanoantimicrobials Progress and Prospects,* Cioffi, N, Rai, M, Eds., Springer: Heidelberg, Dordrecht, London, and New York, 2012, pp. 253–290.
[242] Gupta I, Duran N, Cioffi N. Nano-silver toxicity: emerging concerns and consequences in human health. In *Nano-antimicrobials Progress and Prospects*, Cioffi, N, Rai, M, Eds., Springer: Heidelberg, Dordrecht, London, and New York, 2012, pp. 525–548.
[243] Takami M, Tanaka J, Fujimoto Y. Pleasant fabric. JP2003119649A (2003).
[244] Soejima S, Kijima Y. Antimicrobial synthetic fiber and antimicrobial fiber fabric. JP2004124300A (2004).
[245] Hirakawa S, Nakatsuka H, Takizawa K. Ethylene-vinyl alcohol-based fiber having deodorizing property and antimicrobial property and method for producing the same. JP2007217855A (2007).
[246] Qiuliang C. Antimicrobial deodorization shell fabric. CN202062731U (2011).
[247] Cen R, Mo X, Wang R, Wang X. Antimicrobial fiber, fabric and wound dressing containing nano metal and preparation method thereof. WO2012058962A1 (2012).
[248] Wenge H. Deodorizing antimicrobial fabric. CN102330327A (2012).
[249] Kunimoto N. Antimicrobial nonwoven fabric and its application. JP2006249615A (2006).
[250] Zicheng H, Xidong D, Rong X, Jianglin Z. Medical antimicrobial gauze. CN202459460U (2012).
[251] Jeong G-W. Manufacture method of wet-tissue with antimicrobial and anti-fungus function. US2010180413A1 (2010).
[252] Min Z. Portable sanitary napkin box with antimicrobial and mildew resistant function. CN201071143Y (2008).

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