

Nina PERKAS, Ilana PERELSHTEIN, Aharon GEDANKEN*

Department of Chemistry and Institute for Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat Gan, Israel

* Corresponding author: gedanken@mail.biu.ac.il

COATING TEXTILES WITH ANTIBACTERIAL NANOPARTICLES USING THE SONOCHEMICAL TECHNIQUE

© 2018 Nina Perkas, Ilana Perelshtein, Aharon Gedanken

This is an open access article licensed under the Creative Commons Attribution International License (CC BY)

<https://creativecommons.org/licenses/by/4.0/>**Key words:** sonochemistry, textile, coating, nanoparticles, antibacterial activity.

Abstract: This chapter reviews the research on antibacterial functionalization of textiles with inorganic nanoparticles (Ag, MgO, Al₂O₃) by the sonochemical method. Sonochemistry is one of the most efficient techniques for the synthesis of nanosized materials, wherein ultrasonic waves in the frequency range of 20 kHz to 1 MHz serve as a driving force for chemical reactions. Sonochemical reactions are dependent on acoustic cavitation: the formation, growth, and explosive collapse of bubbles in irradiated liquids. Extreme conditions are developed when the bubbles collapse (temperature >5000 K, pressure >1000 atm, and cooling rates >10⁹ K/sec), resulting in the breaking and forming of chemical bonds.

The deposition of nanoparticles on the surface of natural and synthetic yarns and fabrics (wool, cotton, nylon, polyester) may be achieved using ultrasound irradiation. This process produces a uniform coating of nanoparticles on the textile surface with different functional groups. The coating can be performed by an in situ process, where the nanoparticles are formed and immediately propelled to the surface of the fabric. This approach was demonstrated with nanosilver. Alternatively, the sonochemical process can be used as a "throwing stone" technique, where previously synthesized nanoparticles are sonicated in the presence of the fabric. This process was shown with MgO and Al₂O₃ nanoparticles, which were propelled to the surface by microjets and adhered strongly to the textile without any additional binder. This phenomenon was explained because of the local melting of the substrate due to the high rate and temperature of nanoparticles propelled at the solid surface by sonochemical microjets.

The activity of the fabric finishing with antibacterial nanoparticles was tested against Gram-negative and Gram-positive bacteria cultures. A significant bactericidal effect was demonstrated in both cases, even at a low concentration, below 1 wt.% of nanoparticles in the fabric.

Pokrywanie tkanin nanocząstkami antybakteryjnymi z wykorzystaniem techniki sonochemicznej

Słowa kluczowe: sonochemia, tkanina, powłoka, nanocząsteczki, aktywność przeciwbakteryjna.

Streszczenie: Dokonano przeglądu badań nad funkcjonalizacją antybakteryjną wyrobów włókienniczych nanocząsteczkami nieorganicznymi (Ag, MgO, Al₂O₃) metodą sonochemiczną. Sonochemia jest jedną z najsukcesowniejzych technik syntezy nanomateriałów, w której fale ultradźwiękowe w zakresie częstotliwości od 20 kHz do 1 MHz służą jako siła napędowa dla reakcji chemicznych. Reakcje sonochemiczne są zależne od kawitacji akustycznej: powstawania, wzrostu i wybuchowego rozpadu pęcherzyków w napromieniowanych cieczach. Ekstremalne warunki powstają, gdy pęcherzyki zapadają się (temperatura > 5000 K, ciśnienie > 1000 atm, szybkość chłodzenia > 10⁹ K/s), powodując pękanie i tworzenie wiązań chemicznych.

Osadzanie nanocząsteczek na powierzchni przędz i tkanin naturalnych i syntetycznych (wełna, bawełna, nylon, poliestr) można uzyskać za pomocą napromieniowania ultradźwiękowego. W tym procesie uzyskuje się jednolitą powłokę nanocząsteczek na powierzchni tkaniny z różnymi grupami funkcyjnymi. Powłokę można prowadzić w procesie in situ, w którym nanocząsteczki są formowane i natychmiast wyrzucane na powierzchnię tkaniny. To podejście zostało wykazane z nanosrebrem. Alternatywnie, proces sonochemiczny może być stosowany jako technika „rzucania kamieniami”, w którym wcześniej zsyntetyzowane nanocząsteczki są sonikowane w obecności tkaniny. Proces ten został przedstawiony za pomocą nanocząsteczek MgO i Al₂O₃, które zostały wyrzucane na powierzchnię za pomocą mikrodysz i silnie przylegały do tkaniny bez dodatkowego spoiwa. Zjawisko to tłumaczy się miejscowym topnieniem podłoża z powodu wysokiej szybkości i temperatury nanocząsteczek wyrzucanych na powierzchnię stałą przez sonochemiczne mikrodysze.

Aktywność tkaniny wykończona nanocząsteczkami przeciwbakteryjnymi badano na kulturach bakterii Gram-ujemnych i Gram-dodatnich. Znaczące działanie bakterioobójcze wykazano w obu przypadkach, nawet w niskim stężeniu, poniżej 1% wag. nanocząsteczek w tkaninie.

Introduction

Nanotechnology allows textiles to become multifunctional and produce fabrics with special functions – antibacterial, UV protection, easy cleaning, water- and stain-repellent, and anti-odour [1, 2]. Textile materials, due to their high surface area and ability to retain moisture, are a good media for growth of microorganisms such as bacteria and fungi. Antibacterial finishing of textile is used in hospitals, infant wear, and underwear, and it can provide protection from dangerous infections. Therefore, many studies have been performed in recent years toward improving the antibacterial property of textiles [3, 4]. The advantages of nanomaterials as active antibacterial groups result from their ability to provide high activity using small doses, as their surface area is exceedingly large relative to their size. The application of antibacterial nanoparticles can overcome existing drug-resistance mechanisms, including decreased uptake and increased efflux of drugs from the microbial cell, biofilm formation, and intracellular bacteria [5–7].

Various types of nanomaterials have been developed for treating infectious diseases; however, among all, silver nanoparticles (AgNPs) have proved to be the most effective against bacteria, fungi, viruses, and eukaryotic microorganisms and are exploited in medicine for burn treatment, dental materials, metal coating, and textile fabrics [8–11]. Unfortunately, there are a number of studies indicating that AgNPs are associated with health risks and environmental issues [12–14]. At the same time, many detailed works suggest that the toxicity of AgNPs is caused mainly by leaching of Ag ions and depends on the concentration of silver, particle size, surface structure, and the stability of AgNPs, and their adhesion to the surface of the coated substrate [15–18]. Significant attention was given to improve the international regulation for manufacturing of antimicrobial materials that contain nanosilver [19, 20].

Nowadays, one of the most important research objectives is to achieve a strong adhering of AgNPs to the substrate providing the environmentally friendly application of antibacterial textiles. In order to resolve this issue, various chemical and physical methods were developed. Different combinations of reducing agents (sodium borohydride, hydrazine, glucose, starch) with stabilizers (polyvinyl pyrrolidone, polyethylene glycol, polyvinyl alcohol, thiols) were applied to strengthen the adhesion of nanosilver to the textile [21, 22]. To increase the laundering durability, Zhang et al. deposited AgNPs on silk fabrics by the reaction of silver nitrate with the multi-amino compound RSD-NH₂ [23]. The grafting polymerization of cotton with 2-aminoethyl methacrylate was applied by Liu et al.

to provide excellent laundering durability together with outstanding antibacterial activity, even after 50 accelerated laundering cycles [24]. Babaahmadi et al. reported a novel method for strong encapsulation of AgNPs to polyamide fabric through the reduction of silver nitrate with stannous chloride using cetyltrimethyl ammonium bromide as a stabilizer [25].

Special efforts were put forward to search for green stabilizing agents in order to make the incorporation of silver into textiles an environmentally friendly process [10, 26, 27]. For example, Thomas et al. first attached chitosan molecules to cotton cellulose fabric; Ag (I) ions were incorporated into chitosan layer following by sodium citrate reduction. The NH₂ groups of chitosan acted as a template to bind silver ions, thus providing almost uniform distribution of silver nanoparticles along the fabric surface [28]. In other work, Chattopadhyay et al. modified the cotton fabric with nanochitosan by treatment in acetic acid and stabilization with sodium tripolyphosphate. The modified cotton was treated with nanosilver colloid preliminary prepared by reduction with NaBH₄ in the presence of sodium citrate [29]. A similar approach was applied by Ali et al. for the design of antibacterial polyester [30].

Plasma technology can provide a strong attachment of antibacterial nanoparticles to the textile without any chemical binders, which helps to avoid some environmental problems [22, 26, 31]. For instance, effective antibacterial finishing of cotton and polyester fabrics with nanosilver was performed by Gorensek et al. by the exhaustion plasma method [32, 33]. At the same time, this method requires special equipment and can result in a variety of changes in the surface characteristics, for example, in chemical, electrical, optical, biological, and mechanical properties.

To summarize, most of the existing methods of textile functionalization are based on multistage procedures or complicated physical treatment, such as plasma-enhanced deposition. The conventional coating procedures include preliminary synthesis of NPs by chemical precipitation processes, followed by the application of various templates or binders for anchoring the antibacterial materials to the substrates. Most of the anchoring agents are toxic and can be released into the environment at the coating stage or during exploitation. Therefore, the development of new, effective, and environmentally friendly methods for producing antimicrobial fabrics is highly relevant and important.

Ultrasonic sonochemistry has been proven as a perspective method for coating various types of materials [34]. Sonochemistry studies the chemical reactions that occur under ultrasound irradiation. In liquids, the sound waves generate bubbles that grow in

size until they become unstable. Ultrasonic waves at the frequency range of 20 kHz – 1 MHz are responsible for the process of acoustic cavitation, namely, the formation, growth, and explosive collapse of the bubbles. A number of theories explain how 20 kHz ultrasonic radiation can break chemical bonds [35–37]. One of the theories that explains why, upon the collapse of a bubble, chemical bonds are broken, is the hot spot mechanism [36]. This theory claims that very high temperatures (5,000–25,000 K) are obtained upon the collapse of the bubble. These extreme conditions that developed when the bubbles collapse cause chemical reactions to occur.

The dynamics of cavity growth and collapse during sonication are strictly dependent on the local environment. Cavity collapse in a homogeneous liquid is very different from cavitation near a liquid-solid interface. Suslick and Price [36] demonstrated that microjets and shock waves produced by acoustic cavitation are able to drive metal particles together at sufficiently high velocities to induce melting upon collision. This approach was developed further in our experiments on the deposition of NPs on different types of solid substrates [38]. Typically, the solid substrate is introduced into the sonication cell containing the precursor solution, leading to the fabrication of NPs under the ultrasonic waves. The ultrasonic irradiation passes through the sonication slurry under an inert or oxidizing atmosphere for a specific period of time. This synthetic route is an effective single-step procedure. The microjets formed after the collapse of the bubble propel the just-formed NPs at the surface of the substrate at such a high speed that they adhere strongly to the surface by either physical or chemical interactions, depending on the nature of the substrate – ceramic, polymer, or textile. The excellent adherence of the NPs to the substrate is reflected, for example, in the lack of the leaching of the coated NPs from the substrate surfaces after many washing cycles [39]. Instead of forming the NPs sonochemically, we can purchase them and use ultrasonic radiation just for “throwing stones” at a solid surface. Using this approach, a good adherence is still obtained, but the amount of deposited material on the surface is smaller by a factor of 2–3 [40].

In previous reviews by our group, we described the development of the sonochemical technique for antibacterial finishing of various kinds of textiles with metal nano-oxides and discussed the mechanism of the adherence of NPs to the surface of the substrate [41, 42]. The current chapter is focused on the progress in the sonochemical coating of different kinds of textiles, such as cotton, nylon, polyester, *etc.* with silver nanoparticles by an “in situ” procedure. In addition, the coating of textiles with preliminary synthesized or commercial metal nano-oxides will be considered. The advantages of sonochemistry as a one-step, environmentally friendly method in antimicrobial finishing of textiles will be demonstrated.

1. Sonochemical coating of nylon yarns with silver nanoparticles

Conventionally, the antibacterial finishing of polymer fabrics like nylon-6,6 or polyester with silver nanoparticles consists of the incorporation of nanosilver into the polymer and subsequent application of the nanocomposite as a master batch for the production of polymer yarns [43, 44].

The principal requirements for the synthesis of metal–polymer nanocomposites are small dimensions, regular shape, and uniform size distribution of the metal (silver in this study) nanoparticles. Different methods have been applied for the incorporation of zero-valent silver into polymers, such as in situ polymerization [45], the sol–gel technique [46], and the plasma activation method [47]. Agglomeration of metallic silver can be prevented by adding surfactants such as mercaptosuccinic acid [45], sodium dodecyl sulfonate [48], or amphiphilic hyperbranched macromolecules [49] as stabilizing agents. However, most polymer-based nanocomposites should be exposed to the melt-processing stage and undergo dilution in additional polymeric material to create an industrial polymer product. In the melt-processing and yarns extrusion stages, interaction with the stabilizing agent can cause undesirable transformations like the destruction and aggregation of the nanosilver. Therefore, synthesis of well-dispersed silver–polymer nanocomposites is very important when preparing nylon fibres with antibacterial properties.

Using an ultrasound-assisted method, Gedanken et al. produced a silver-nylon nanocomposite by a polyol reduction in a single stage [50]. The sonochemical synthesis was performed in an aqueous solution of silver nitrate in the presence of ammonia and ethylene glycol (EG) as reducing agent. The optimal ratio of ammonia to silver was found to be 2:1, corresponding to the formation of $[\text{Ag}(\text{NH}_3)_2]^+$ complex as an intermediate reaction product. It was also found that, in addition to serving as a polyol reducing agent, EG also promotes anchoring of the silver nanoparticles to the surface of the nylon by interacting with the surface functional groups.

The XRD patterns of the product demonstrated that the silver deposited on the nylon was crystalline in nature, and the diffraction peaks match those of the cubic silver phase in the joint committee on powder diffraction standards (JCPDS) database – powder diffraction file (PDF) No. 4-783. The scanning electron microscopy (SEM) method provides an image of the silver particles distribution on the nylon surface (Figure 1). The polymer is uniformly coated with silver nanoparticles 50–60 nm in diameter. Large agglomerates were not observed on the composite surface, indicating that there was no agglomeration when the silver was anchored to the surface of the nylon.

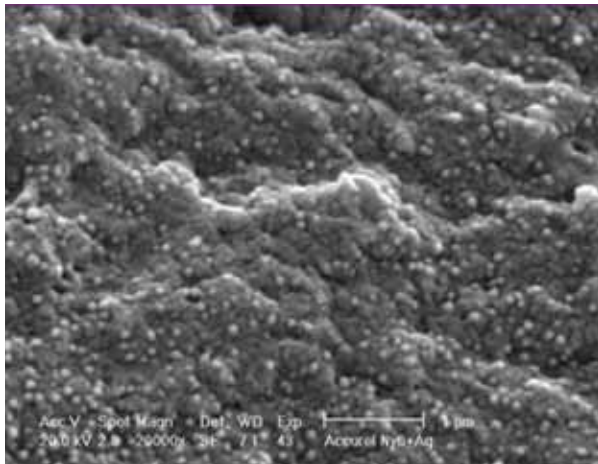


Fig. 1. SEM image of nylon surface coated with silver

The bubbles created during sonochemical irradiation of the liquid collapsed near the surface of the solid substrate. The resultant microjets and shock waves promoted the fast migration of silver nanoparticles formed during the sonication process to the nylon surface. The silver nanoparticles impinge on the nylon surface at such high speed that they might cause its melting. Consequently, the particles adhere strongly to the surface. We also attribute the strong bonding of the silver particles to the surface to their interaction with functional groups of the nylon 6,6, which prevents the aggregation of the particles. Because of the very high speed at which the particles are propelled at the surface, the smaller silver particles of about 20 nm in size are able to penetrate the surface and are distributed inside the polymeric grain (Figure 2).

The information concerning the silver–nylon interaction was obtained from optical and Raman spectroscopy. The nanocrystalline silver-coated polymer displays an optical reflectance spectrum due to collective surface plasma resonance. This optical property

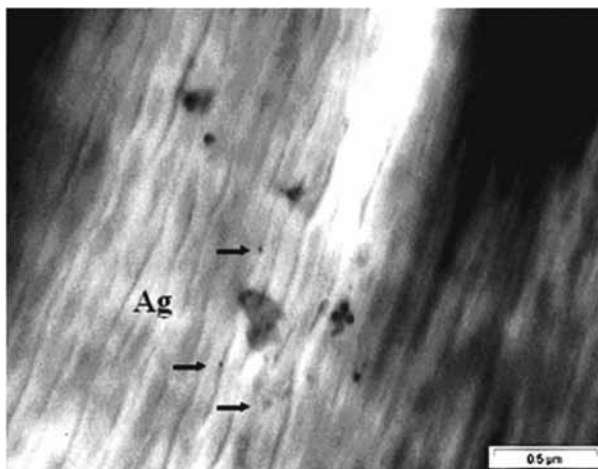


Fig. 2. Transmission electron microscopy (TEM) image of silver–nylon composite (cut-off section).

is sensitive to many factors, such as the geometry parameters, microstructure, and the interaction with the surrounding matrices. The diffuse reflectance spectra (DRS) of silver particles collected from the solution after the sonication process and of the silver–nylon composite shows a reflection peak centred at 330 nm (Figure 3). The location of this peak in DRS is strongly blue-shifted in comparison with the usually registered optical reflection of silver nanoparticles at about 400 nm [51]. However, the appearance of a silver absorption–reflection peak at about 320–330 nm with a simultaneous decrease in the intensity of the 400 nm band is not new and was already reported in [52], where the large blue shift was attributed to the diminution in silver particle size. A similar DRS spectrum was obtained for nanocrystalline silver with a particle size of 50 nm [53].

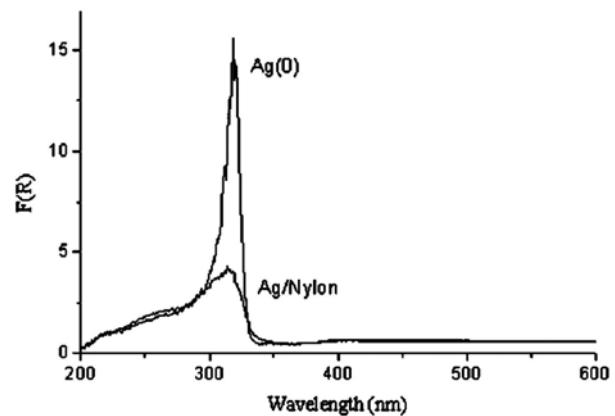


Fig. 3. Diffuse reflection spectra of a silver–nylon composite

Raman spectroscopy was also used to characterize the silver-nylon nanocomposites. The bands at 1344 and 1580 cm^{-1} observed in the Raman spectra of the coated nylon (Figure 4) are assigned to pristine carbon. These peaks are absent in the original polymer beads. It is well known that the surface-enhanced Raman scattering

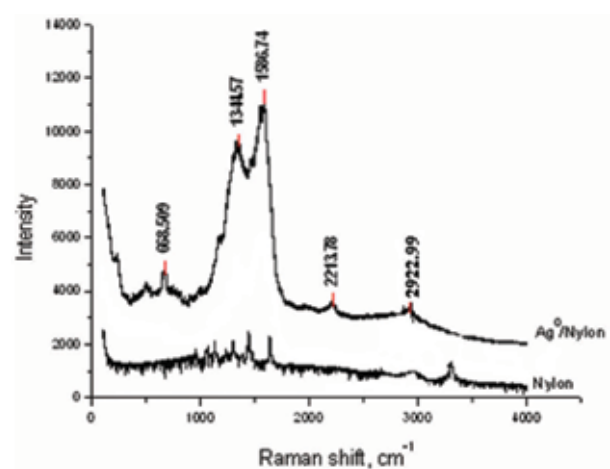


Fig. 4. Raman spectra of nylon beads and silver–nylon composite

(SERS) resulting from the deposition of silver colloids on pure carbon is widely used for characterizing carbon materials, as it makes the carbon vibration modes Raman-active [54, 55]. Thus, it seems reasonable that the appearance of high-intensity bands characteristic of carbon after coating nylon with nanosilver were caused by localized melting of the polymer at the points of contact with the silver nanoparticles, which results from the SERS effect of silver deposition on carbon materials.

The silver-nylon nanocomposite containing 1 wt.% of silver was used as a master batch for spinning nylon 6,6 27/7 (decitex/filaments) partially-oriented yarn (POY). The POY melt-spinning process is a well-known technology for producing manmade yarn. Nylon, polyester, and other synthetic yarns are manufactured by this method. The pellets of the master batch were combined with a stream of neat nylon 6,6 pellets at the feed hopper and were thus diluted to the required concentration in the yarn. The silver-nylon master batch was mixed with pure nylon to reduce the silver concentration to a level of 0.1 wt. % Ag. The fabric was knitted from this yarn on a one-feed knitting machine.

The standard antimicrobial test demonstrated the high efficiency of the silver-nylon composite against microorganisms. The log reduction test showed that the four-level bacterial number dropped after 18 h. These results are applicable to Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Pseudomonas aeruginosa*) bacteria strains. The silver-coated nylon composite was exposed to several washing procedures in water at elevated temperatures (60–80°C). The silver concentration did not change, even after 10 washing cycles. These results demonstrate the high stability of the silver coating on nylon, a unique property of sonochemical coating.

2. Sonochemical deposition of nanosilver on natural wool fibres

Natural wool fibres under proper temperature and humidity are a very good media for the generation and propagation of microorganisms [56]. Antibacterial treatment of natural fibres is of particular interest, because it significantly increases their functional performance. Wool fibres as proteins consist of polar groups of amino acid residues which can bind other charged organic and inorganic molecules. The cationic amine salts can interact with anionic acidic groups in acid dyes to form ionic pairs, thus colouring the wool fibres. Similarly, the carboxylic acid groups in wool

proteins are also interactive with many other functional groups.

The wool fibres of merino type were treated with a sulphur nano-silver colloidal solution (SNSE) containing an Ag/S complex. It was demonstrated that the finished wool fabrics with sulphur nanosilver colloid had various functionalities, such as moth proofing and antibiotic and antistatic properties [57]. In other work, the nanoparticle-wool composite was produced by the reduction of silver ions in solution by trisodium citrate (TSC) in the presence of merino wool fibres or fabrics. The Ag⁰ nanoparticles simultaneously bind to the amino acids of the keratin protein in the wool fibres using TSC as a linker. The colours of the resulting merino wool-silver nanoparticle composites range from yellow/brown to red/brown and also to brown/black due to the SERS effect of silver. In addition to these optical effects, the silver nanoparticle-wool composites exhibit effective antimicrobial activity, thus inhibiting the growth of microbes, and also an increase in the electrical conductivity, imparting antistatic properties to the fibres [58]. The silver deposition on wool was also performed by the impregnation of the wool in a water/alcohol solution of silver. The wet substrates were then exposed to UV-rays to induce the formation of metal silver clusters on the surface of the material. The antibacterial activity, as well as the stability and durability of the coating, were demonstrated; however, the method is limited by the conditions of exposing the materials to UV rays [59].

We demonstrated the deposition of silver nanoparticles on wool by the coating of neat fibres with silver nanoparticles via ultrasound irradiation. The process was performed in a one-step sonochemical procedure with a slurry containing wool fibres and silver nitrate in water/EG medium (9/1) with the addition of ammonia in a ratio to silver of 2:1 [60]. The produced silver-coated wool fabrics maintained the high flexibility and elasticity typical of wool. Studies of the silver-coated wool fibres by physical and chemical methods demonstrated the presence of highly dispersed silver nanoparticles (~5 nm) incorporated into the natural wool (Figure 5). Some of the silver particles aggregate into clusters located at the fibre crossovers.

X-ray photoelectron spectroscopy (XPS) studies demonstrated that silver nanoparticles are attached to the keratin fibres as a result of the interaction between sulphur and either Ag⁺ or Ag clusters. These sulphur atoms most likely originate from the partial disconnection of the S-S bond in the keratin fibres. The stability of the coating is satisfactory: Even after 10 cycles of thermal treatments and simulated laundering, no change in silver concentration was detected.

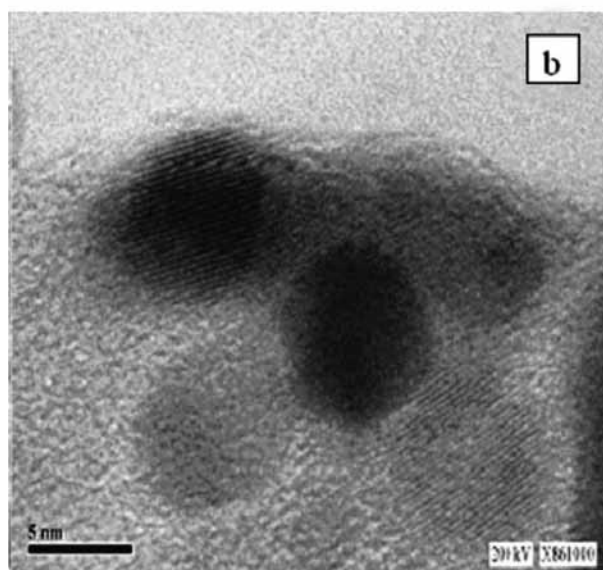
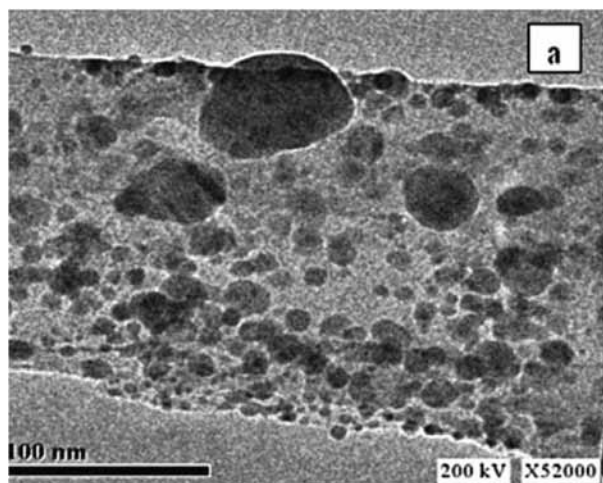


Fig. 5. High-resolution TEM (HRTEM) images of (a) silver-coated wool fiber and (b) individual particles on the surface of the wool fibre

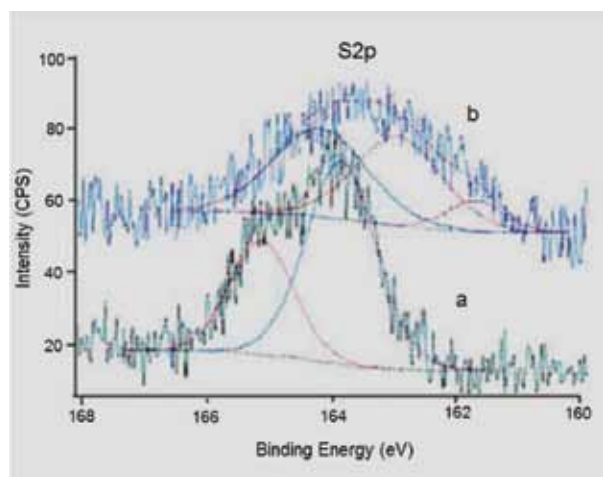


Fig. 6. XPS spectra of (a) neat and (b) silver-coated wool

3. Sonochemical coating of silver nanoparticles on textile fabrics (nylon, polyester and cotton) and their antibacterial activity

The ultrasound-assisted coating of fibres and yarns with nanosilver was further developed for antibacterial coating of different types of textiles [61]. The process was performed by ultrasound radiation in a one-step reaction procedure and did not involve any toxic binders. It was the first report on the deposition of silver nanoparticles on fabrics using the sonochemical method.

One of the aims of the study was to investigate the interaction between the fibre surface and the metallic silver as a result of the sonochemical irradiation, which are the options that can result from the sonication are formation of a chemical bond between the silver and the functional groups of the substrate and physical adsorption of the silver nanoparticles on the surface of the fabric. We performed experiments on three types of fabrics: nylon, polyester, and cotton. These fabrics differ in their functional groups, which are amide, ester, and alcohol, respectively. All fabrics were exposed to the same reaction conditions: reagent concentration, reaction time, temperature, and sonication power. The silver content deposited on the three different fabrics was nearly the same. This result indicated that the amount of deposited silver was independent of the nature of the substrate. It also indicated that, most probably, the mechanism of coating by ultrasound irradiation does not involve the formation of new bonds between the silver and the functional groups of the substrate. We can therefore conclude that the coating is, in fact, a physical adsorption of the nanoparticles on the substrate as a result of the sonication.

The sonochemical irradiation of a liquid causes two primary effects – cavitation and heating. When the microscopic cavitation bubbles collapse near the surface of the solid substrate, they generate powerful shock waves and microjets that cause effective stirring/mixing of the liquid. The after-effects of the cavitation are several hundred times greater in heterogeneous systems than in homogeneous systems [35]. In our case, the ultrasound waves promote fast migration of the newly formed silver nanoparticles to the fabric surface. This might cause a local melting of the substrate surface, which is the reason that the particles strongly adhere to the fabric surface, regardless of its properties. The high-resolution SEM (HR-SEM) micrographs of cotton fibres before and after deposition of Ag nanoparticles demonstrated the smooth structure of bare cotton fabric and the homogeneous deposition of silver nanoparticles on the cotton yarns (Figure 7). The higher magnification image indicates the average size of the nanosilver deposited on the cotton. Note, however, that some aggregates consisting of small particles were also observed.

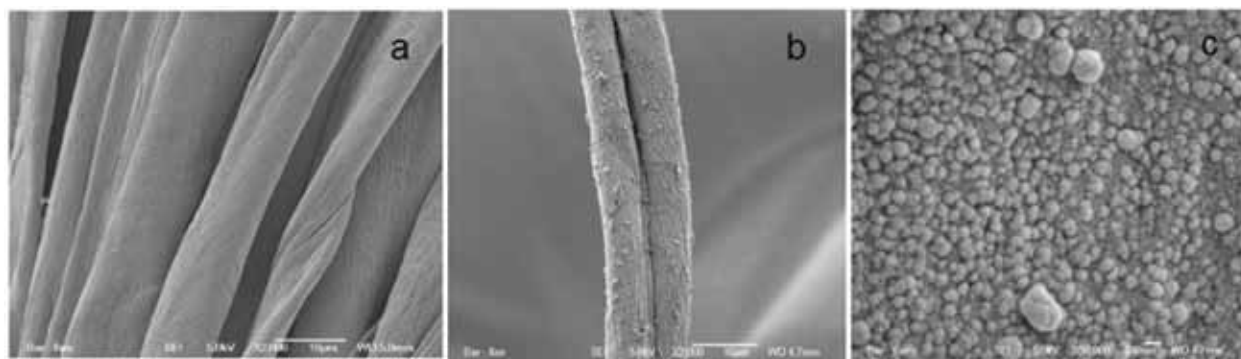


Fig. 7. HR-SEM images of (a) pristine fibres and (b) fabrics coated with Ag nanoparticles, shown in (c) at high magnification (x50000)

To elucidate the distribution of silver NPs in the textile, the Rutherford backscattering spectrometry - particle-induced X-ray emission (RBS-PIXE) analysis was applied. The RBS analysis is based on elastic collisions between ions and the atomic nucleus, wherein the slowing down of ions in matter provides depth information. The PIXE analysis is based on the ionization of the inner shells of atoms. Combined scanning micro-PIXE-RBS analysis, where the ion probe is focused to a micrometre level and scanned over the sample, allows one to obtain the lateral distribution of elements [62]. Two regions of Ag coating were selected for RBS analysis. It was found that the Ag thickness layer can vary by about 30% (between 138 and 94 at cm^{-2}). The Ag profile distribution from the outer surface to the cotton fibre showed that few atomic percent of Ag, i.e. 3–4 at.%, were present inside the fibre as deep as several hundred nanometres (Figure 8).

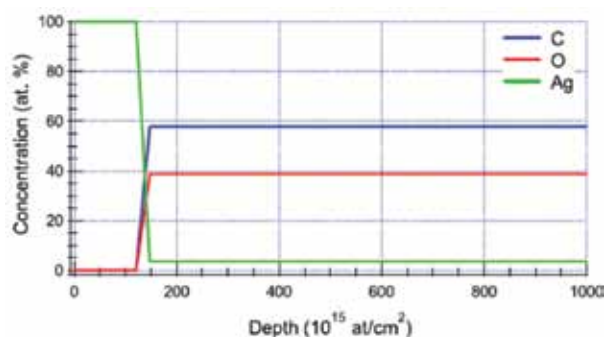


Fig. 8. Profile of elements on cotton as a function of depth

The tensile mechanical properties of the silver-coated fabric were studied on a universal testing machine, Zwick 1445. Fabric samples folded four times with a gauge length of 60 mm and a width of 40 mm were placed in special grips. The silver-coated samples showed a rather more brittle behaviour compared to the pristine fabric. Ultimately, the tensile strength of the coated sample was $\sim 10\%$ lower than the pristine sample. The observed changes in the mechanical behaviour of

the yarn were in a range that is acceptable for standard cotton fabrics. According to this result, one can conclude that the sonochemical treatment of the fabric did not cause any significant damage to the structure of the yarn.

The antibacterial activity of the coated cotton fabric was demonstrated against both gram-negative *Escherichia coli* and gram-positive *Staphylococcus aureus* strains that were eradicated completely after 1 h of treatment with the 6 wt% Ag-coated fabric, and after approximately 1.5 h of treatment with the sample coated with 1 wt% Ag. It was found that the diffusion of silver ions from the deposited silver nanoclusters to the saline was very slow, and only a small part of the total amount of silver can participate in antibacterial activity. The maximal possible silver concentration in the saline solution was 0.13 or 0.78 mg ml^{-1} from the fabrics containing 1 and 6 wt.% of silver, respectively. Nevertheless, even the total possible amount of silver is much less than the minimum inhibitory concentration (MIC) in a solution that is commonly used in commercial preparations (10 mg ml^{-1}) [63]. More likely, the observed required time of 1.5 h to reduce the initial amount of colony forming unit (CFU) to zero is due to the velocity of Ag^+ ions, which are responsible for the antibacterial activity. Thus, the sonochemically prepared silver-coated fabrics exhibit excellent antibacterial properties, probably due to the high association of the Ag nanoparticles with the membrane.

4. Sonochemical coating technique as a “throwing stones” method

The deposition of magnesium oxide and aluminium oxide NPs on fabrics in a one-step sonochemical reaction is not possible. The sonication of M-acetate ($\text{M} = \text{Mg}, \text{Al}$) leads to amorphous phases of corresponding M-hydroxides. Antibacterial tests towards *Staph. aureus* and *E. coli* show that these M-hydroxides possess no bactericidal activity. Only the heating of the amorphous product to high temperatures of up to several hundred

degrees allows the formation of crystalline nano-oxides. This action is not possible when the nanoparticles are deposited on textiles, because the textile will be destroyed at such temperatures. In our study, we applied the ultrasound irradiation as a "throwing stones" technique for deposition of commercial MgO or Al_2O_3 NPs on the textile. Namely, commercial nanopowders of MgO and Al_2O_3 (both < 50 nm) were sonicated in the presence of the cotton fabric [40]. When the suspension of preliminary synthesized nanoparticles and the fabric were irradiated, the microjets formed after the collapse of the acoustic bubble "threw" the nanoparticles as "stones" at a high speed to the cotton yarns. This use of ultrasound irradiation for coating differs from our previous studies, where the nanoparticles of Ag, CuO, and ZnO were formed from the precursor solution under ultrasound irradiation and subsequently propelled to the solid surface by the microjets. The main difference between the one and two-stage methods is the amount of material that is deposited. The anchored amount for the commercial NPs was found to be smaller by a factor of 2–3 as compared to the one-stage deposition due to the fact that not all the particles were pushed by the microjets to the fabric surface. Nevertheless, using ultrasound as a "throwing stones" technique is an efficient process, especially for nanoparticles that cannot be synthesized sonochemically.

MgO is known to have a strong antibacterial activity [64, 65]. Different methods were reported on the synthesis of magnesium oxide NPs, such as a controlled speed of formation following the heating procedure [64], microwave-assisted synthesis [66], the formation of MgO from aqueous droplets in a flame spray pyrolysis reactor [67], and sonochemically-enhanced hydrolysis followed by supercritical drying [68]. However, we are not aware of any information in the literature related to the deposition of magnesium oxide on textiles.

One of the aims of this research was to reach a minimal effective concentration of the deposited metal oxide NPs on the fabrics, which still demonstrate an antibacterial activity. Optimal conditions, such as reaction time, the type of solvent, and the amounts of reagents were found in order to obtain a high quality coating. To confirm that the structure of the MgO nanoparticles was not damaged during sonication, a control experiment was carried out, namely, the magnesium oxide nanopowder was sonicated under the same reaction conditions as with the fabric, and the powder was centrifuged and dried at the end of reaction. The XRD patterns of sonochemically-treated MgO nanoparticles demonstrate that the magnesium oxide is crystalline in nature, and the diffraction peaks match a cubic phase of MgO (PDF No. 004-0829). The peaks at $2\theta = 42.9, 62.3, 74.67, \text{ and } 78.61^\circ$ are assigned to the (200), (220), (311), and (222) reflection lines of cubic MgO, respectively. No peaks that are a characteristic of any impurities were detected.

The morphology of the fibre surface before and after the deposition of magnesium oxide nanoparticles was studied by HR SEM, and a homogeneous deposition of nanoparticles on the cotton yarn was observed (Figure 9). The nanoparticles of 20–30 nm in size are well distributed along the fibres, but some aggregation can be observed.

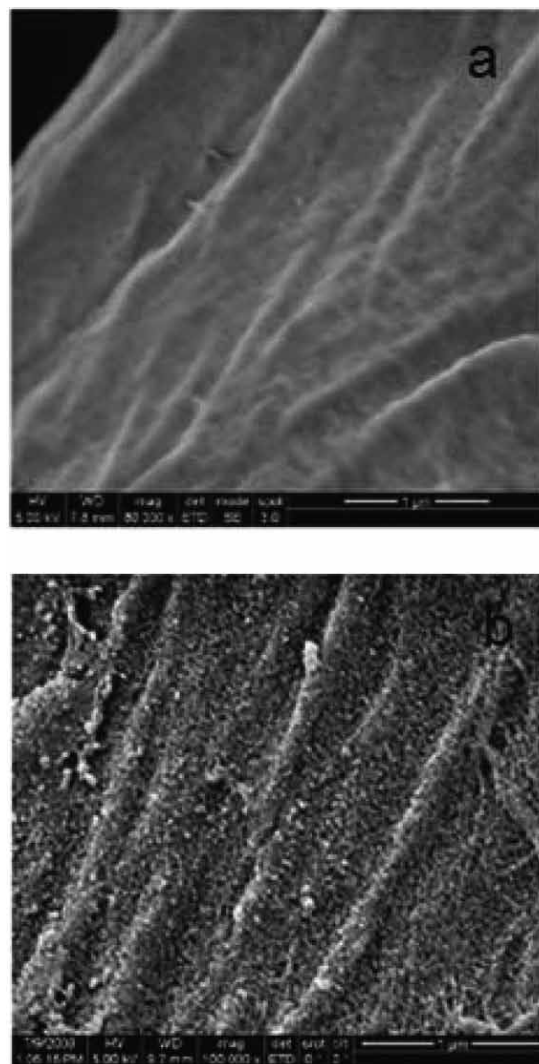


Fig. 9. SEM images of (a) pristine cotton bandage and (b) MgO-coated bandage

A more detailed analysis was performed for the Al_2O_3 -coated fabric. Before the sonochemical coating reaction, the commercial aluminium oxide nanopowder was tested by XRD, and a single crystalline phase of orthorhombic $\delta\text{-Al}_2\text{O}_3$ was detected (PDF No. 046-1215). In order to study the influence of the ultrasound on the structure of the nanoparticles, a high resolution transmission electron microscope (HRTEM) was used with ultramicrotome cutting. For this purpose, the cotton fibres were embedded in the copper grid, using the epoxy embedding technique. The HRTEM of the Al_2O_3 -coated fabric is depicted in Figure 10a, and

a uniform distribution of the particles along the fibre is observed. The red-marked particle in Figure 10a was taken under high magnification (Figure 10b) providing further verification for the identification of the coating as Al_2O_3 . The distances measured between the (131), (220), and (311) lattice planes were 0.25, 0.28, and 0.25 nm, respectively, which match very well the distances reported in the literature for the orthorhombic lattice of $\delta\text{-Al}_2\text{O}_3$ (PDF No. 046-1215). These results indicate that ultrasound irradiation can be used as an effective method for coating textiles without causing any damage to the crystalline structure of the commercial nanoparticles.

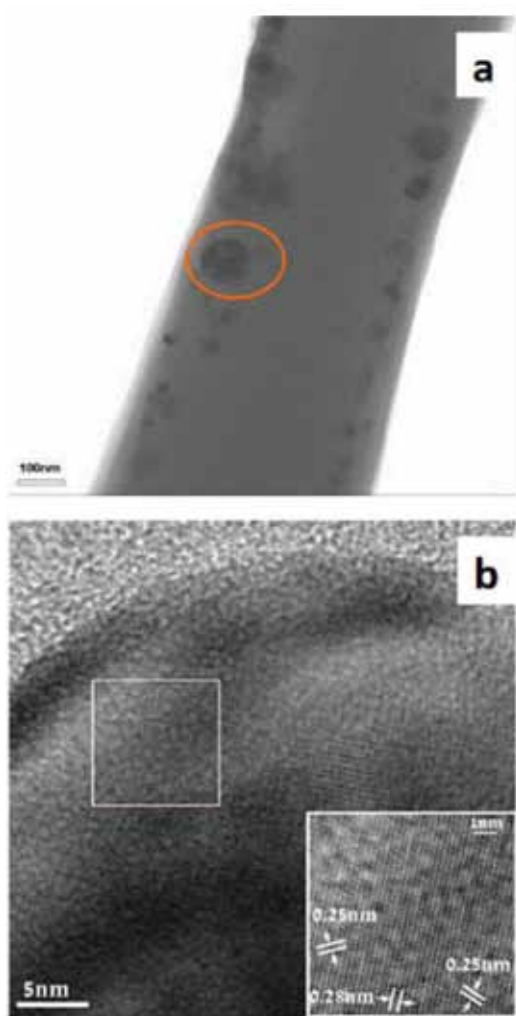
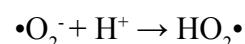


Fig. 10. HRTEM of (a) Al_2O_3 -coated bandage showing (b) high magnification ($\times 1\text{M}$) of the red-marked particle

The antibacterial activity of cotton fabrics coated with 0.8% of MgO was determined using the Gram-positive *Staph. aureus* and Gram-negative *E. coli* bacteria strains. The treatment for one hour with MgO-coated cotton caused complete growth inhibition of *E. coli*. Regarding *S. aureus*, a 100% reduction in viability was reached after 3 hours, while, after 1 hour, a reduction

of 90% could be seen. As for Al_2O_3 , it was evident that alumina NPs possess milder antimicrobial properties, namely, 84% growth inhibition of *E. coli* in 3 hours and 23% growth inhibition in 1 h. Regarding *Staph. aureus*, only 75% growth inhibition was observed in 3 hours, and only about 11% growth inhibition was found after one hour of treatment.

The chemoluminescence method showed that the dominant reactive oxygen species (ROS) generated on MgO surfaces were superoxide anions [69]. As mentioned above, these ROS are not very reactive themselves to bacterial cells; however, these species are in equilibrium, as shown in the following reaction:



When $\bullet\text{O}_2^-$ species are generated near the bacterial membrane during the respiratory process, hydroperoxyl radicals ($\text{HO}_2\bullet$) are produced. The $\text{HO}_2\bullet$ radicals are much more reactive than $\bullet\text{O}_2^-$ and are able to penetrate the cell membrane. This concept is supported by the fact that contact between bacterial cells and MgO powders is important for MgO-induced bacterial death. Moreover, as a consequence of this contact, a local alkaline effect due to basic sites on MgO surfaces may also enhance the antibacterial activity of MgO [70].

The obtained results confirm that the sonochemical method is effective for the production of antibacterial fabrics, irrespective of the mode of nanoparticle deposition, i.e. the NPs may be created in the sonochemical reaction and simultaneously deposited, or they may undergo sonochemical-assisted deposition following preliminary synthesis.

Conclusions

This chapter demonstrates the ability of the sonochemical coating technique to impart properties to various substrates including polymers, wool, and synthetic textiles. Herein the effective antibacterial properties of the substrate were demonstrated by coatings with silver nanoparticles. The coating can be applied either on finished products such as textiles or on a polymeric level and further extruded for obtaining the desired product. The coatings were performed by a simple, efficient, one-step procedure using environmentally friendly reagents. Physical and chemical analyses demonstrated that the nanocrystals are finely dispersed onto the surfaces without any significant damage to the structure of yarns. The strong adhesion of the metal nano-oxides to the substrate was demonstrated by the absence of leaching of the NPs into the washing solution after 65 washing cycles. The washed coated textiles showed high antibacterial activity. The presented technique was already proven to be scalable and can be further implemented in industry for the production of functional nanocomposites.

References

1. Patra J.P., Gouda S.: Application of nanotechnology in textile engineering: An overview. *Journal of Engineering and Technology Research*, 2013, 5(5), pp. 104–111.
2. Yetisen A.K., Qu H., Manbachi A., Butt H., Dokmeci M.R., Hinestroza J.P., Skorobogatiy M., Khademhosseini A., Yun S.H.: Nanotechnology in textile. *ACS Nano*, 2016, 10, pp. 3042–3068.
3. Morais D.S., Guedes R.M., Lopes M.A.: Antimicrobial approaches for textiles: from research to market. *Materials*, 2016, 9, pp. 498–519.
4. Wu Y., Yang Y., Liu H., Yao X., Leng F., Chen Y., Tian W.: Long-term antibacterial protected cotton fabric coating by controlled release of chlorhexidine gluconate from halloysite nanotubes. *RSC Advances*, 2017, 7, pp. 18917–18925.
5. Singh R., Smitha M.S., Singh S.P.: The role of nanotechnology in combating multi-drug resistant bacteria. *Journal of Nanoscience and Nanotechnology*, 2014, 14, pp. 4745–4756.
6. Pelgrift R.Y., Friedman A.J.: Nanotechnology as a therapeutic tool to combat microbial resistance. *Advanced Drug Delivery Reviews*, 2013, 65, pp. 1803–1815.
7. Beyth N., Hourri-Haddad Y., Domb A., Khan W., Hazan R.: Alternative antimicrobial approach: Nano-antimicrobial materials. *Evidence-Based Complementary and Alternative Medicine*, 2015, art. 246012.
8. Rai M., Yadav A., Gade A.: Silver nanoparticles as a new generation of antimicrobials. *Biotechnology Advances*, 2009, 27(1), pp. 76–83.
9. Zille A., Almeida L., Amorim T., Carneiro N., Esteves M.F., Silva C.J., Souto A.P.: Application of nanotechnology in antimicrobial finishing of biomedical textiles. *Materials Research Express*, 2014, 1, art. 032003.
10. Gokarneshan N., Velumani K.: Application of nano silver particles on textile materials for improvement of antibacterial finishes. *Global Journal of Nanomedicine*, 2017, 2(3), art. 555586.
11. Pietrzak K., Gutarowska B., Machnowski W., Mikołajczyk U.: Antimicrobial properties of silver nanoparticles misting on cotton fabrics. *Textile Research Journal*, 2016, 86(8), pp. 812–822.
12. Kim K.T., Truong L., Wehmas L., Tanguay R.L.: Silver nanoparticle toxicity in the embryonic zebrafish is governed by particle dispersion and ionic environment. *Nanotechnology*, 2013, art. 115101.
13. Gaillet S., Rouanet J.M.: Silver nanoparticles: Their potential toxic effects after oral exposure and underlying mechanisms – A review. *Food and Chemical Toxicology*, 2015, 77, pp. 58–63.
14. León-Silva S., Fernández-Luqueño F., López-Valdez F.: Silver nanoparticles (Ag NPs) in the environment: a review of potential risks on human and environmental health. *Water Air Soil Pollution*, 2016, 227(9), art. 306.
15. Marambio-Jones C., Hoek E.M.V.: A review of the antibacterial effects of silver nanomaterials and potential implications for human health and the environment. *Journal of Nanoparticle Research*, 2010, 12(5), pp. 1531–1551.
16. Levard C., Hotze E.M., Lowry G.V., Brown G.E.: Environmental transformations of silver nanoparticles: Impact on stability and toxicity. *Environmental Science & Technology*, 2012, 46, pp. 6900–6914.
17. Chernousova S., Eppe M.: Silver as antibacterial agent: Ion, nanoparticle, and metal. *Angewandte Chemie International Edition*, 2012, 51, pp. 2–20.
18. Rivero P.J., Urrutia A., Goicoechea J., Arregui F.J.: Nanomaterials for functional textiles and fibers. *Nanoscale Research Letters*, 2015, 10, pp. 501–522.
19. FDA: Centers & Offices. [Online]. 2009. [Accessed 15 November 2018]. Available from: www.fda.gov/AboutFDA/CentersOffices
20. Faunce T., Watal A.: Nanosilver and global public health: international regulatory issues. *Nanomedicine*, 2010, 5(4), pp. 617–632.
21. Dastjerdi R., Montazer M.: A review on the application of inorganic nano-structured materials in the modification of textiles: focus on antimicrobial properties. *Colloids Surf. B Biointerfaces*, 2010, 79, pp. 5–18.
22. Simoncic B., Klemencic D.: Preparation and performance of silver as an antimicrobial agent for textiles: A review. *Textile Research Journal*, 2016, 86, pp. 210–223.
23. Zhang G., Liu Y., Gao X., Chen Y.: Synthesis of silver nanoparticles and antibacterial property of silk fabrics treated by silver nanoparticles. *Nanoscale Research Letters*, 2014, 9, art. 216.
24. Liu H., Lv M., Deng B., Li J., Yu M., Huang Q., Fan C.: Laundering durable antibacterial cotton fabrics grafted with pomegranate-shaped polymer wrapped in silver nanoparticle aggregations. *Scientific Reports*, 2014, 4, art. 5920.
25. Babaahmadi V., Montazer M.: A new route to synthesis silver nanoparticles on polyamide fabric using stannous chloride. *Journal of the Textile Institute*, 2015, 106, pp. 970–977.
26. Palza H.: Antimicrobial polymers with metal nanoparticles. *International Journal of Molecular Sciences*, 2015, 16, pp. 2099–2116.
27. Xu Q.B., Xie L.J., Diao H., Li F., Zhang Y.Y., Fu F.Y., Liu X.D.: Antibacterial cotton fabric with enhanced durability prepared using silver nanoparticles and carboxymethyl chitosan. *Carbohydrate Polymers*, 2017, 177, pp. 187–193.

28. Thomas V., Bajpai M., Bajpai S.K.: In situ formation of silver nanoparticles within chitosan-attached cotton fabric for antibacterial property. *Journal of Industrial Textiles*, 2011, 40(3), pp. 229–245.
29. Chattopadhyay D., Inamdar M.S.: Improvement in properties of cotton fabric through synthesized nano-chitosan application. *Indian Journal of Fibre & Textile Research*, 2013, 38, pp. 14–21.
30. Ali S.W., Rajendran S., Joshi M.: Synthesis and characterization of chitosan and silver loaded chitosan nanoparticles for bioactive polyester. *Carbohydrate Polymers*, 2011, 83(2), pp. 438–446.
31. Shahidi S., Ghoranneviss M.: Plasma sputtering for fabrication of antibacterial and ultraviolet protective fabric. *Clothing and Textiles Research Journal*, 2016, 34, pp. 37–47.
32. Gorenšek M., Gorjanc M., Bukošek V., Kovač J., Petrović Z., Puač N.: Functionalization of polyester fabric by Ar/N₂ plasma and silver. *Textile Research Journal*, 2010, 80, pp. 1633–1642.
33. Gorjanc M., Bukošek V., Gorenšek M., Mozetič M.: CF₄ plasma and silver functionalized cotton. *Textile Research Journal*, 2010, 80, pp. 2204–2213.
34. Gedanken A.: Doping nanoparticles into polymers and ceramics using ultrasound radiation. *Ultrasonics Sonochemistry*, 2007, 14, pp. 418–430.
35. Suslick K.S.: The chemical effect of ultrasound. *Scientific American*, 1989, 260, pp. 80–86.
36. Suslick K.S., Price G.J.: Application of ultrasound to materials chemistry. *Annual Review of Materials Research*, 1999, 29, pp. 295–326.
37. Mason T.J.: *Sonochemistry*. London: Royal Society of Chemistry Press, 1990.
38. Gedanken A., Perkas N.: *Sonochemical coatings of nanoparticles on flat and curved ceramic and polymeric surfaces*. In: Rizzo M., Bruno G. (Eds.): *Surface Coatings*. Nova Science Publishers Inc., 2009, pp. 213–236.
39. Perelshtein I., Ruderman E., Perkas N., Beddow J., Singh G., Vinatoru M., Joyce E., Mason T.G., Blanes M., Molla K., Gedanken A.: The sonochemical coating of cotton withstands 65 washing cycles at hospital washing standards and retains its antibacterial properties. *Cellulose*, 2013, 20, pp. 1215–1221.
40. Perelshtein I., Applerot G., Perkas N., Grinblat J., Hulla E., Wehrschetz-Sigl E., Hasmann A., Guebitz G.M.: Ultrasound radiation as a “throwing stones” technique for the production of antibacterial nanocomposite textiles. *ACS Applied Materials & Interfaces*, 2010, 2, pp. 1999–2004.
41. Perkas N., Gedanken A., Wehrschuetz-Sigl J., Guebitz G.M., Perelshtein I., Applerot G.: *Innovative inorganic nanoparticles with antibacterial properties attached to textiles by Sonochemistry*. In: Altavilla C., Enrico C. (Eds.): *Inorganic Nanoparticles: Synthesis, Applications, and Perspectives*. CRC Press, 2011, pp. 367–391.
42. Perelshtein I., Perkas N., Gedanken A.: *Making the hospitals a safer place by the sonochemical coating of textiles by antibacterial nanoparticles*. In: Grumezescu A. (Ed.): *Surface Chemistry of Nanobiomaterials: Applications of Nanobiomaterials*. Elsevier Inc., 2016, pp. 71–102.
43. Chae D.W., Oh S.G., Kim B.C.: Effect of silver nanoparticles on the dynamic crystallization behavior of nylon-6. *Journal of Polymer Science Part B: Polymer Physics*, 2004, 42, pp. 790–799.
44. Damerchely R., Yazdanshenas M.E., Rashidi A.S., Khajavi R.: Morphology and mechanical properties of antibacterial nylon 6/nano-silver nano-composite multifilament yarns. *Textile Research Journal*, 2011, 81, pp. 1694–1701.
45. Choi S.H., Lee K.P., Park S.B.: Preparation and characterization of poly(ester)-silver and nylon-silver nanocomposites. *Studies in Surface Science and Catalysis*, 2003, 146, pp. 93–96.
46. Mahltig B., Haufe H., Bottcher H.: Functionalisation of textiles by inorganic sol-gel coatings. *Journal of Materials Chemistry*, 2005, 15, pp. 4385–4398.
47. España-Sanchez B.L., Avila-Orta C.A., Neira-Velazquez M.G., Solis-Rosales S.G., Gonzalez-Morones P.: Preparation of polymer nanocomposites with enhanced antimicrobial properties. *MRS Proceedings*, 2013, 1479, pp. 57–62.
48. Kvitek L., Panáček A., Soukupová J., Kolář M., Večeřová R., Prucek R., Holecová M., Zboril R.: Effect of surfactants and polymers on stability and antibacterial activity of silver nanoparticles (NPs). *Journal of Physical Chemistry C*, 2008, 112, pp. 5825–5834.
49. Aymonier C., Schlotterbeck U., Antonietti L., Zacharias P., Thomann R., Tille J.C., Mecking S.: Hybrids of silver nanoparticles with amphiphilic hyperbranched macromolecules exhibiting antimicrobial properties. *Chemical Communications*, 2002, 24, pp. 3018–3019.
50. Perkas N., Amirian G., Dubinsky S., Gazit S., Gedanken A.: Ultrasound-assisted coating of nylon 6,6 with silver nanoparticles, and its antibacterial activity. *Journal of Applied Polymer Science*, 2007, 104(3), pp. 1423–1430.
51. Carotenuto G.: Synthesis and characterization of poly(*N*-vinylpyrrolidone) filled by monodispersed silver clusters with controlled size. *Applied Organometallic Chemistry*, 2001, 15, pp. 344–351.
52. Karpov S.V., Basko A.L., Popov A.K., Slabko V.V.: Optical spectra of silver colloids within the framework of fractal physics. *Colloid Journal*, 2000, 62(6), pp. 699–713.
53. Taneja P., Ayyub P., Chandra R.: Size dependence of the optical spectrum in nanocrystalline silver. *Physical Review B*, 2002, 65, pp. 245412–245418.

54. Roy D., Barber Z.H., Clyne T.W.: Ag nanoparticle induced surface enhanced Raman Spectroscopy of chemical vapor deposition diamond thin films prepared by hot filament chemical vapor deposition. *Journal of Applied Physics*, 2002, 91(9), pp. 685–6088.
55. Xu B., Lu Y.: Chemical modification and surface reactions on carbon fibers studied by SERS. *Journal of Raman Spectroscopy*, 2006, 37, pp. 1423–1426.
56. Cardamone J.M.: Biodeterioration of wool by microorganisms and insects. *Bioactive Fibers and Polymers*, 2001, 16, pp. 293–298.
57. Ki H.Y., Kim J.H., Kwon S.C., Jeong S.H.: A study on multifunctional wool textiles treated with nano-sized silver. *Journal of Materials Science*, 2007, 42(19), pp. 8020–8024.
58. Kelly F.M., Johnston J.H.: Colored and functional silver nanoparticle-wool fiber composites. *ACS Applied Materials & Interfaces*, 2011, 3(4), pp. 1083–1092.
59. Pollini M., Paladini F., Licciulli A., Maffezzoli A., Nicolais L., Sannino A.: Silver-coated wool yarns with durable antibacterial properties. *Journal of Applied Polymer Science*, 2012, 125, pp. 2239–2244.
60. Hadad L., Perkash N., Gofer Y., Calderon-Moreno J., Ghule A., Gedanken A.: Sonochemical deposition of silver nanoparticles on wool fibers. *Journal of Applied Polymer Science*, 2007, 104, pp. 1732–1737.
61. Perelshtein I., Apperlot G., Perkash N., Guibert G., Mikhailov S., Gedanken A.: Sonochemical coating of silver nanoparticles on textile fabrics (nylon, polyester and cotton) and their antibacterial activity. *Nanotechnology*, 2008, 19, art. 245705.
62. Bertrand M., Weber G., Schoefs B.: Metal determination and quantification in biological material using particle-induced X-ray emission. *TrAC Trends in Analytical Chemistry*, 2003, 22, pp. 254–262.
63. Chun-Nam L., Chi-Ming H., Rong C., Qing-Yu H., Wing-Yiu Y., Hongzhe S, Kwong-Hang T.P., Jen-Fu C., Chi-Ming C.: Silver nanoparticles: partial oxidation and antibacterial activities. *JBIC Journal of Biological Inorganic Chemistry*, 2007, 12, pp. 527–534.
64. Huang L., Li D.Q., Lin Y.L., Wei M., Evans D.G., Duan X.: Controllable preparation of nano-MgO and investigation of its bactericidal properties. *Journal of Inorganic Biochemistry*, 2005, 99, pp. 986–993.
65. Ohira T., Kawamura M., Iida Y., Fukuda M., Yamamoto O.: Influence of the mixing ratio on antibacterial characteristics of MgO-ZnO solid solution in two phase coexistence region. *Journal of the Ceramic Society of Japan*, 2008, 116, pp. 1234–1237.
66. Makhluף S., Dror R., Nitzan Y., Abramovich Y., Jelinek R., Gedanken A.: Microwave-assisted synthesis of nanocrystalline MgO and its use as a bactericide. *Advanced Functional Materials*, 2005, 15, pp. 1708–1715.
67. Seo D.J., Park S.B., Kang Y.C., Choy K.L.: Formation of ZnO, MgO and NiO nanoparticles from aqueous droplets in flame reactor. *Journal of Nanoparticle Research*, 2003, 5, pp. 199–210.
68. Stengl V., Bakardjieva S., Marikova M., Bezdicka P., Subrt J.: Magnesium oxide nanoparticles prepared by ultrasound enhanced hydrolysis of Mg-alkoxides. *Materials Letters*, 2003, 57, pp. 3998–4003.
69. Sawai J., Kojima H., Igarashi H., Hashimoto A., Shoji S., Sawaki T., Hakoda A., Kawada E., Kokugan T., Shimizu M.: Antibacterial characteristics of magnesium oxide powder. *World Journal of Microbiology and Biotechnology*, 2000, 16, pp. 187–194.
70. Ardizzzone S., Bianchi C.L., Vercelli B.: MgO powders: interplay between adsorbed species and localization of basic sites. *Applied Surface Science*, 1998, 126, pp. 169–175.