Chapter 11
Engineering Nanostructured Silver Coatings for Antimicrobial Applications

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11.1 Introduction

The interest in nanotechnologies is growing worldwide thanks to the enormous number of publications devoted to the fundamental aspects of nanosciences. Physiology, industrial bioprocessing, biology and medicine represent just some examples of the areas for nanotechnology application [1, 2]. Compared with silver metal, silver nanoparticles are known for their higher antimicrobial activity, due to their high specific surface area [3] and the large surface to volume ratio [4], against a broad spectrum of bacteria and also against drug-resistant bacteria [5], fungi [6], and viruses [7–9]. The use of silver nanoparticles incorporated into various categories of consumer products, such as cosmetics, clothes, electronics, aerospace, textiles, and medicines, is growing thanks to the interesting and unique properties they confer to the product due to their nanometric size [10, 11]. This is a very important matter related to the emergence of an increased number of microbial organisms resistant to multiple antibiotics and the continuing emphasis on health care costs [12].

In hospital practice, the risk of infection associated with the use of indwelling medical devices is very high [13], and many cases of morbidity and mortality have been reported [14]. Microorganisms commonly attach to the surface of indwelling medical devices forming a biofilm [15, 16] that is, by definition, an accumulation of microorganisms and of their extracellular products forming a structured community highly resistant to antimicrobial treatment and tenaciously bound to the surface [17]. Many strategies have been employed to reduce this problem, among them one

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approach for prevention is the use of antimicrobials which can be incorporated into, or used to coat, medical polymeric devices like catheters [18]. Heparin coatings on catheters and stents [19, 20], the use of chlorhexidine and silver sulfadiazine coatings [21] and also the use of silver nanoparticles have been demonstrated to be efficacious against bacterial proliferation [22, 23]. As shown in Fig. 11.1, many uses of silver and silver nanoparticles can be applied in medicine. Silver can be used to stop epistaxis and post-traumatic granulomas, to improve skin regeneration and for its antibacterial and anti-inflammatory effects. The use of silver nanoparticles in medicine is related to their prophylactic environmental and antibacterial effect in bone cement and implants, for venous catheters and neurosurgical shunts [24].

In hospitals, in addition to the treatment of medical devices, silver represents a promising instrument for advanced textile for wound dressing [24–26], antiseptic bandages [27], for hospital gowns, flax and for surgical masks, in particular when the replacement cannot always be done immediately [28], in order to prevent infections and generation of bad odors. Textiles, in fact, can easily become carriers of fungi and bacteria [29], so the use of silver can also be helpful in treatment of skin diseases [30] and to ensure a major degree of hygiene and daily welfare. Silver treatment can be applied according to two different methods: the first is the insertion of silver nanoparticles as host inside the textile matrix [31], while in the second silver is applied as a coating on the material [32].

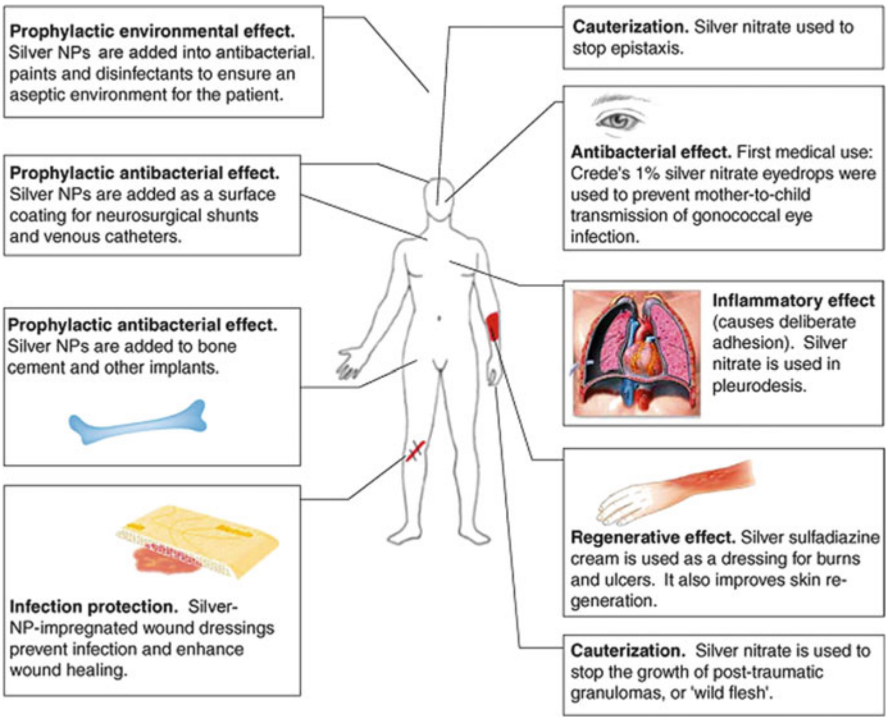

Fig. 11.1 Uses of silver (*right*) and silver nanoparticles (*left*) in medicine (Adapted from [24])

The innovative technology presented in this paper is a surface engineering process, an interesting alternative to more expensive ways of silver deposition and a very effective technique to treat many different types of substrates. Three case studies will be explored, that is textile, temporary medical devices and artificial leather. For each type of substrate, the method of silver deposition chosen for the specific application will be explored and the characterization of samples will be discussed.

11.2 Past and Present Uses of Antimicrobial Silver

The antimicrobial spectrum of silver is exceptionally broad against fungi [6], viruses [7–9] and bacteria [5]. Panacek et al. demonstrated the antifungal activity of silver nanoparticles against pathogenic *Candida* [6]; Lu et al. hypothesized that the direct interaction between silver nanoparticles and Hepatitis B virus double-stranded DNA or viral particles is responsible for their antiviral mechanism [8]; a study carried out by Feng et al. on *Escherichia coli* and *Staphylococcus aureus* suggested that morphological and structural changes in bacterial cells, the formation of small electron-dense granules around the cell wall and the inactivation of bacterial proteins occur after addition of Ag^+. DNA loses its replication ability once the bacteria have been treated with silver ions [24, 33]. Figure 11.2 summarizes

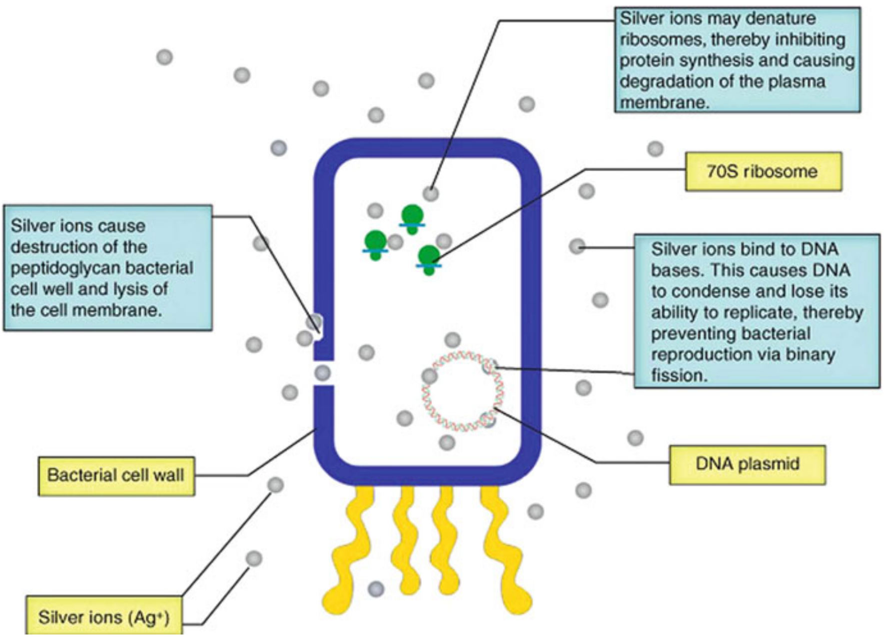

Fig. 11.2 Mechanisms of the antibacterial activity of silver ions (Adapted from [24])

some possible mechanisms of action of silver ions in a schematic bacterial cell, like the interactions of silver ions with peptidoglycan cell wall, plasma membrane, bacterial (cytoplasmic) DNA, and bacterial proteins [24].

Silver and its antimicrobial properties are known since antiquity. Herodotus, the Greek philosopher and historian, described the use of silver for water purification; Pliny the Elder, the famous Roman physician, reported the properties of silver in 79 AD in his encyclopedia *Natural History* in which he wrote that silver was extremely effective in causing wounds to close [34]; Hippocrates, the father of modern medicine, believed silver powders to have a beneficial healing effect for ulcers [35].

Since the nineteenth century, many studies have been carried out and many applications of silver have been employed in different fields of medical research [36]. In 1884, in Germany, Carl Siegmund Franz Credé introduced an eye prophylaxis to prevent ocular infection by using silver nitrate solution on neonates [25]. In the 1920s, colloidal silver was accepted by the US Food and Drug Administration (FDA) as being effective for wound management [37] and through the first half of the twentieth century it was used in controlling infection in burn wounds [25]. In the 1940s, penicillin was introduced as a healing method and antibiotics became the standard treatment for bacterial infections, so the use of silver diminished [37, 38]. The resistance of pathogenic bacteria to many antibiotics and the growing interest in nanotechnologies and nano-sized materials have led to many technological advances of nano-sized silver and to the development of many applications, such as coatings for medical devices, silver dressings, silver coatings on textile fabrics [36, 39], water sanitization [40] and so on. Today, also NASA uses silver to purify drink water in space flights [25].

11.3 Review of Nanosilver Coating Deposition Methods and Properties

Many procedures have been developed for the synthesis of Ag nanoparticles (NPs) [41] and several methods have been described in order to obtain thin silver coatings. The biological activity and the interaction of silver nanoparticles with bacteria depend on their size [22] and shape [42]. Morones et al. studied the interaction of silver nanoparticles with different types of Gram-negative bacteria. Their results demonstrated the dependence of the antibacterial capability both on concentration of particles and on their size [22]. Pal et al. investigated the antibacterial capability of silver nanoparticles synthesized in different shapes (truncated triangular, spherical, rods) against *Escherichia coli*. They demonstrated that the reactivity of silver particles changes as a function of their shapes, probably due to the really effective surface area in terms of active facets [42]. The results of their research are shown in Figs. 11.3 and 11.4. Images obtained by energy-filtering transmission electron microscopy (EFTEM) of silver NPs with different shapes are shown in Fig. 11.3.

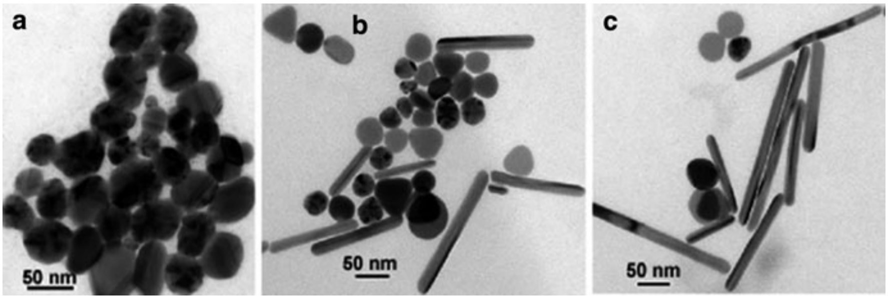

Fig. 11.3 EFTEM images of silver nanoparticles. (**a**) Spherical nanoparticles synthesized by citrate reduction. (**b**) Silver nanoparticles of different shapes. (**c**) Purified rod-shaped nanoparticles (From [42])

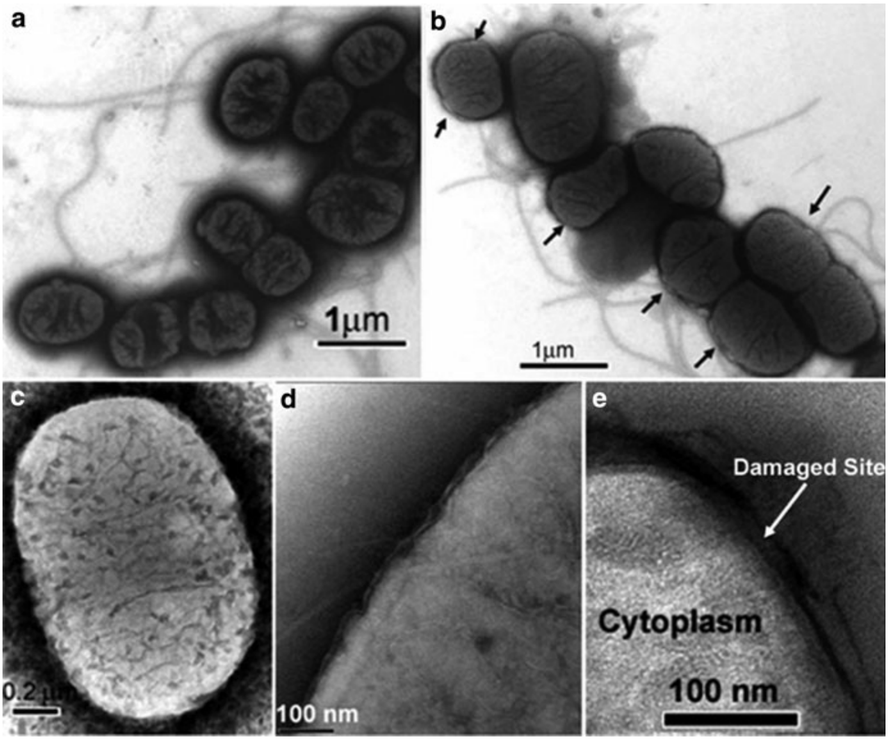

Fig. 11.4 EFTEM images of *E. coli* cells. (**a**) Untreated *E. coli*. (**b**) *E. coli* grown on agar plates supplemented with AgNO3. (**c**) *E. coli* treated with triangular silver nanoplates. (**d**) *E. coli* treated with spherical silver nanoparticles. (**e**) Enlarged image of part of the bacterial cell membrane treated with triangular silver nanoparticles (Adapted from [42])

The effect obtained against a bacterial cell of *Escherichia coli* after treatments with $AgNO_3$, triangular and spherical silver nanoparticles are shown in Fig. 11.4, where both the partial (Fig. 11.4b) and multiple (Fig. 11.4e) damages on bacterial membrane and also the presence of dark irregular pits on the cell surface are visible, compared with untreated *E. coli*.

Nanostructured materials incorporated into larger mesoscopic and macroscopic systems and the enhancing of coating functionality and coating process represent a crucial key in the success of nanotechnology in many different applications [43]. Surface modification is very effective in the interactions with biological systems. A relevant strategy widely used in biomedical research consists in modifying the material surface by plasma treatment, such as plasma etching, plasma deposition, plasma polymerization and so on, in order to modify material surfaces without altering bulk properties of the material [44]. Plasma processes can also be combined with colloidal lithography, a patterning technique used to texture surfaces with nanofeatures and some recent research on plasma-aided micro- and nanostructuring processes for biomedical applications have been reported by Sardella et al. [45]. Gomathi et al. provided an overview of recent advances in biomedical applications of plasma surface-modified polymers [46]. Korner et al. described the combination of deposition of plasma polymer coatings with embedded Ag nanoparticles and the sputtering of Ag atoms from an Ag target, with incorporation of Ag nanoparticles in the growing polymer matrix [47]. The deposition of plasma coatings using combined deposition/etching/sputtering processes enabled the formation of multi-functional surfaces [48].

Among techniques for the deposition of silver coatings, the use of magnetron sputtering combined with atom beam source has been demonstrated to be effective for coatings on thermally sensitive polymeric substrates [49]. Magnetron sputtering, already tried on substrates like SiO_2, polypropylene and nonwoven fabrics to fix Ag nanoparticles has also been used by Mejıa et al. to produce cotton–Ag composites [50]. Nanostructured silver films were deposited at room temperature on polypropylene non-woven by radio frequency magnetron sputter coating to obtain the antibacterial properties. The relationship between sputter parameters and antibacterial properties were investigated by Wang [51, 52]. He found that both the antibacterial capability and the grain size depend on the deposition time, while no effect of sputtering power and argon pressure have been discovered during his experiments.

Another method for textile modification is the sol–gel technique for preparing bioactive materials for biomedical applications [53]. Antimicrobial coatings for textile based on silver-containing silica have been developed by Mahltig et al. The release of biocides from these coatings and the biocidal effect can be controlled by modifying the content of the biocide in the silica sol [54]. An alternative method to constrain silver in nanodimensions reported in the literature is the loading of zeolite with silver ions [55].

In addition to the most commonly applied dip-coating methods, sonochemical coating using ultrasound irradiation as well as the sputter deposition of Ag NPs onto textile surfaces were performed [44]. The sonochemical irradiation of wool fibers in an aqueous solution of silver nitrate containing ethylene glycol under a reducing atmosphere of an argon/hydrogen gas mixture resulted in the coating of the neat wool fibers with silver nanoparticles [56]. Perelshtein et al. have described a process carried out by ultrasound radiation in a one-step reaction procedure to obtain nylon, polyester and cotton with antibacterial properties [57]. The chemical reduction method involves the reduction of $AgNO_3$ by a reducing agent in the presence of a suitable stabilizer, which is necessary in protecting the growth of silver particles through aggregation. In the formation of silver nanoparticles by the chemical reduction method, the size and aggregation of silver nanoparticles are affected by various parameters, such as initial $AgNO_3$ concentrations, reducing agent/$AgNO_3$ molar ratios, and stabilizer concentrations [58]. Nair and Laurencin provided an overview about the synthesis of silver nanoparticles by the reduction of a silver salt and their stabilization, both in solution and on surfaces, with particular attention to biomedical applications [59].

Microwave irradiation [60], electrochemical synthesis [61] and photo-reduction [62] have also been proposed to obtain silver nanoparticles.

11.4 In Situ Photoreduction and Deposition of Silver Metal Clusters

The researchers of University of Salento (Lecce, Italy) have developed, and patented in 2004, a new technique based on the photo-reduction of silver ions in the form of nanoparticles directly on the substrate [63]. A spin-off company, Silvertech Ltd, has been started in 2008 to promote the technology transfer. The technique is suitable for many different substrates, natural or synthetic, from textile to medical devices, making them antibacterial with a very cheap process. The antibacterial treatment of the substrate is obtained by impregnating natural or synthetic substrates with an alcoholic solution, a photo-reducing agent and a silver salt, and afterwards by exposing them to UV rays until the silver ions are reduced to metal silver. Methanol is not only the solvent but also the reducing agent that activates the photo-reduction process on the surface. The amount of methanol used for this purpose is strictly related to the amount of silver used for the treatment. The solution can be prepared also using different solvents such as water or ethanol. The only requirement is that the molar ratio methanol/silver nitrate is more than one. The effect of the in situ reduction of silver ions consists of a strong antibacterial coating made of neat silver clusters. Silver nanoparticles do not form inside the solution after the mixing of precursor and solvent; they form as a consequence of UV exposure directly on the substrate to which they bond strongly, independently of the nature of the substrates and of the way of deposition.

The photochemical reaction on which the process is based is the following:

$$Ag_n + Ag^+ + CH_3 \cdot OH + h\nu \Rightarrow Ag_{n+1} + H^+ + CH_2O$$

In order to obtain information about the size of silver nanoparticles and about the lattice parameters of silver, transmission electron microscopy, TEM, has been

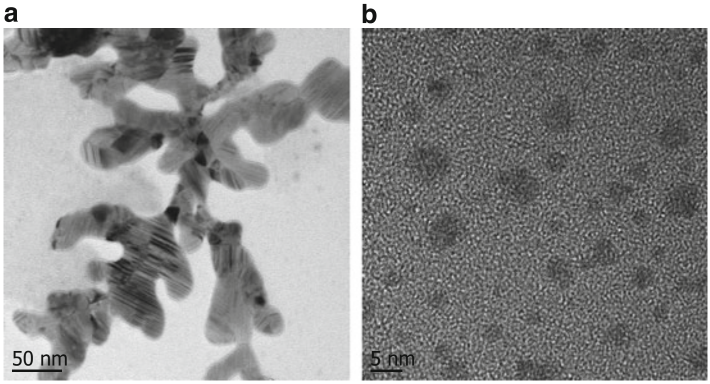

Fig. 11.5 TEM images obtained from silver solution deposited on carbon-covered copper grid, showing an extensive crystal structure (**a**) and a good distribution of small nanoparticles (**b**)

performed. Images obtained by TEM analysis of coatings made of a solution of silver salt and alcohol deposited onto a carbon-covered copper grid are reported in Fig. 11.5. They show the presence of both extensive crystal structures and very small silver particles with a size of about 2–3 nm; the identified lattice parameters (lattice fringes of 2.36 Å) correspond to metallic silver and in particular to atomic planes {111}.

According to the specific application to which the substrate is destined, it is possible to modify the composition of the silver solution and the mechanism of deposition, according to costs and to the degree of antibacterial effect to be achieved. For example, silver-coated textiles for daily use realized to improve the degree of hygiene and for personal care do not require a very high degree of antimicrobial activity; silver-coated medical devices instead need a very high antibacterial capacity to reduce the risk of infections.

In this chapter, some examples of applications joined by the common needs of hygiene and control of the bacterial proliferation and the results obtained by the characterization of the treated substrates will be shown and discussed. The application fields of Silvertech technology chosen to be exposed as case studies are textiles, temporary medical devices and artificial leather.

11.4.1 Silver Deposition on Fibers and Textile

The deposition of silver on textile fibers and fabrics represents a very interesting way to confer antibacterial properties to textile materials that can be used in fields of application that require a high degree of hygiene and the control of bacterial proliferation. For example, the introduction of silver in hospital textiles, such as cotton or flax used for sheets of patients or gowns for nurses and doctors, can represent an effective instrument to contain the diffusion of diseases. In addition, there are many other applications of silver-treated textiles in the sector of daily comfort. Textile with antimicrobial properties used for the production of common knitwear or underwear can guarantee to customers a major welfare benefit by reducing unpleasant odors caused by bacterial proliferation in corporeal areas most exposed to perspiration. Cotton textile was selected for silver deposition because it is a substrate suitable both for medical field and common clothing. Cotton is made up of many short fibers (1–3 cm) with flattened and irregular sections. Their extension and contraction occurring by the absorption of humidity can irritate the skin [64] and an excellent environment for microorganisms to grow can develop owing to their ability to retain moisture [65]. Colonization of several types of bacteria, especially *Staphylococcus aureus*, represents the most common complication in patients affected by atopic dermatitis (AD) [66], a chronic disease of pruritus and eczematous lesions [67]. In the treatment of AD, various solutions have been tried, among them antibacterial drugs or topical steroids, or the use of special textiles with the antimicrobial capability to contain bacterial colonization [68]. Daeschlein et al. investigated in patients affected by AD the bacterial contamination in textiles containing silver versus placebo and in particular the effect of silver textiles on *S. aureus* and total bacteria colonizing the skin of AD patients. The obtained data were in agreement with those of Gauger et al. [69], who found a significant decrease in *S. aureus* on the skin of AD patients when they wore a silver textile [70].

Various methods, depending on the particular active agent and fiber type, have been developed to confer antimicrobial activity to textiles. For synthetic fibers, the antimicrobial active agents can be incorporated into the polymer prior to extrusion or blended into the fibers during their formation [71] and during the melt spinning. There are numerous ways by which antimicrobial properties can be accomplished in textiles: incorporation of volatile and non-volatile antimicrobial agents directly into fibers, coating or adsorbing antimicrobials onto fiber surfaces, immobilization of antimicrobials to fibers by ion or covalent linkages, and the use of fibers that are inherently antimicrobial [72]. To produce commercial silver-coated nylon fabrics, 12% by weight of silver is added during manufacturing by an electroless plating process [73], while the antimicrobial capability of nylon substrates coated with metallic silver has been checked against *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Candida albicans* [74].

Silvertech technology, cheap and effective because it implies the treatment of only the surface of the material, has been adopted both for synthetic yarn and natural yarn [32]. Different deposition methods, like impregnation, dipping or spraying, related to the nature of the substrate and the amount of silver solution required have been developed. As provided by the technology, after the deposition of the solution on the substrate, the UV irradiation occurs with consequent synthesis of silver nanoparticles firmly bonded to the substrate, so the wet yarns are exposed to strong lamps in special containers for this treatment. Here, mild reducing conditions are applied for the treatment of cotton, all involving a silver salt and a reducing agent. In some cases, fiber pretreatment after improved silver adhesion is also proposed. The comparison between a silver-treated textile substrate and an

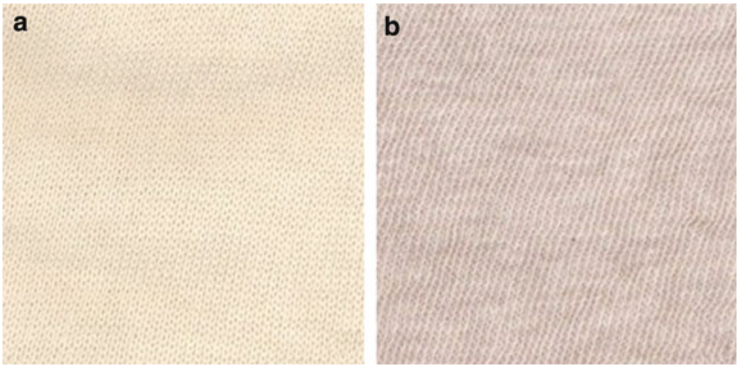

Fig. 11.6 Visual comparison of untreated cotton (**a**) and silver-treated cotton (**b**)

untreated one is shown in Fig. 11.6, in which the turning brown color of the treated sample due to the presence of silver nanoparticles is clearly visible.

The method of deposition chosen to deposit silver on textile was nebulization. As explained above, all samples have been washed before testing in order to remove unreacted silver salt. In textile, furthermore, this is not the only reason. In fact, it is necessary to ensure the presence of silver also after many washings, to check that silver nanoparticles exert their benefits for a very long time despite the user conditions. For this purpose, samples of cotton have been subjected to washing up to 20 times and they have been tested before and after washings with respect both to microscopy and the antibacterial activity. Images obtained by scanning electron microscopy (SEM) are shown in Fig. 11.7. The presence of nanometric particles on the surface of the treated sample that are not present on the untreated sample is clearly visible. The treated sample reveals a quite uniform distribution of silver on the surface and the very small size of the particles that sometimes aggregate in clusters of larger dimensions, even after 20 industrial washings.

The antibacterial activity of silver-treated cotton was checked before and after washings according to standard 'SNV 195920-1992', which is an agar diffusion test that relates the antibacterial capability to the dimension of the bacterial inhibition zone around the treated samples. The results of the Agar diffusion tests are shown in Fig. 11.8, in which the differences between the untreated sample and the silver-treated one are clearly visible. It is possible to assert that there are no great differences between the unwashed treated sample and the washed treated one because the bacterial inhibition growth area is very similar in the two cases. This confirms that washings do not reduce the benefits induced by treatment thanks to the very firmly bonded silver coating.

Another confirmation of this matter lies in the quantitative study of the amount of silver on the surface of the sample, carried out by thermogravimetric analysis (TGA) on unwashed and washed silver-treated samples. TGA is a testing that records the change in the weight of the sample as a function of the increasing

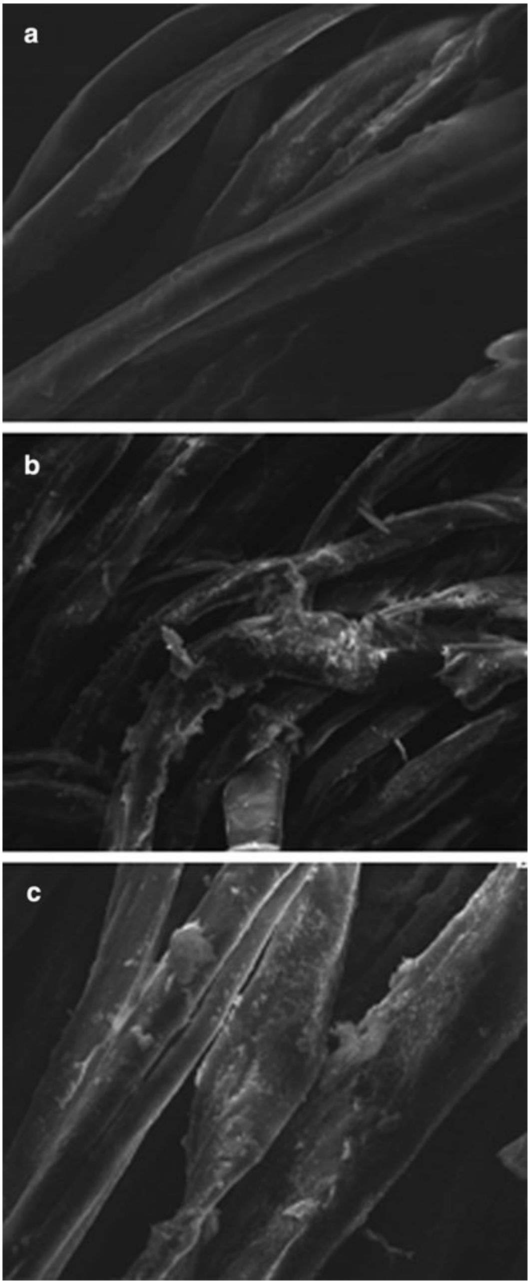

Fig. 11.7 SEM images obtained from untreated cotton fibers (**a**), silver-treated cotton fibers (**b**) and silver-treated cotton fibers after 20 industrial washings (**c**)

temperature. The comparison between the TGA data of an untreated sample and a silver-treated sample leads to the quantification of silver as the incombustible solid residue at 900°C, the temperature to which all the substrate has burnt. These

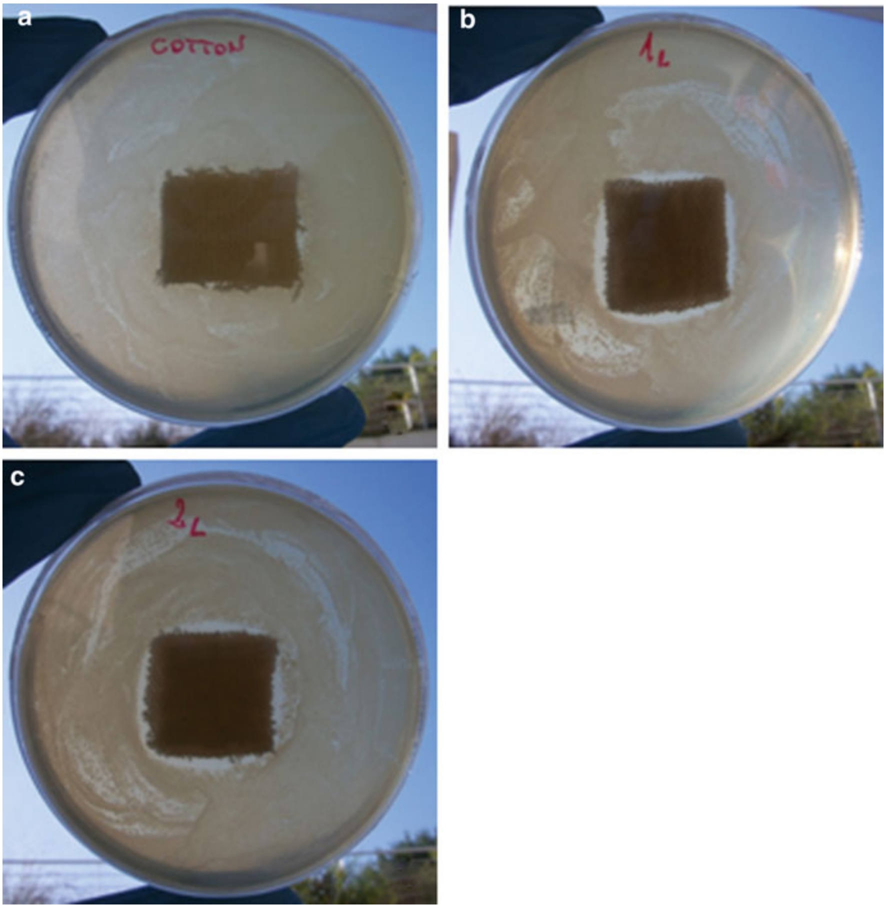

Fig. 11.8 Test of *Escherichia coli* growth on the sample of silver-treated cotton before washings (**b**) and after washings (**c**) in comparison with the untreated one (**a**)

results are shown in Table 11.1, in which the calculated amount of silver is reported for each substrate used in the case studies. The results have not revealed any significant differences between washed and unwashed cotton samples, being 2.72 wt% the amount of silver for the unwashed sample and 2.42 wt% for the sample washed 20 times. That means that washings do not remove silver nanoparticles from the substrate.

11.4.2 Silver Deposition on Catheters

The risk of infections associated with the use of indwelling medical devices is very high. In particular, bloodstream infections deriving from catheterization are

Table 11.1 Data collected by TGA analysis reporting the amount of silver for each type of silver-treated substrate

Substrate	Silver content (wt%)
Untreated cotton yarn	–
Silver-treated cotton yarn	2.72
Silver-treated cotton yarn after 20 washings	2.42
Untreated catheter	–
Silver-treated catheter	0.51
Untreated synthetic leather	–
Silver-treated synthetic leather	3.08

reported as one of the major cause of morbidity and mortality in hospitalized patients [75]. This happens because of the formation of bacterial biofilm growing on the surface of the device with consequent proliferation of infection [76]. So, it is very important to avoid the growth of bacteria on the surface of the device. For this purpose many strategies have been employed to reduce dialysis catheter-related infections, such as the impregnation in antibiotic and antiseptics, or the use of substances containing silver [77].

Biological responses to polymeric materials depend basically on surface chemistry and structure. So the surface modification of biomaterials is carried out to retain the key physical properties with modification of the outermost surface to influence bio-interaction. The surface modification techniques include physical/chemical methods, such as physical deposition of coatings, grafting or chemical modification, and biological methods, such as protein adsorption or immobilization of biomolecules [78]. A technology developed at the University of Erlangen provides for the impregnation of the entire catheter with a distribution of billions of silver nanoparticles (0.8–1.5 wt%) in the catheter matrix (polyurethane, silicone) on a carrier, preferably barium sulphate [40, 79].

The silver nanoparticles distributed on the carrier surfaces can be dispersed in a polymer matrix by thermoplastic processing [80]. Serghini-Monim et al. reported the results of adsorption of a silver complex on plasma-modified polyurethane surface performed to confer antibacterial properties to catheters. The purpose of the plasma modification treatment was to increase the concentration of adsorption sites for a chemical vapor deposition (CVD) reaction and to increase the surface biomedical compatibility through the incorporation of amine groups to mimic amino acids [81].

The method of silver deposition developed by Silvertech and the University of Salento for these medical devices consists of the treatment of the inner and outer surface of the catheter because it is subjected to the risk of contamination on both sides. Temporary double lumen polyurethane “Carbothane” catheters 30 cm long and with an outer diameter of 4 mm were coated. They penetrate into the jugular vein with a length of 10–15 cm and remain in contact with the blood stream inside and outside the lumina for about 30 days for acute dialysis and blood filtration. To ensure a good deposition of silver coating on the polymeric surface of catheters, the method of deposition chosen for this particular purpose is the dipping of the device into the silver solution, made for this application only by silver salt and alcohol. The reason for these choices, about the deposition technique and the composition of the solution, derives from visual considerations about the color. That must be more uniform as possible in the final product. The treatment in this case consists of dipping the catheters in the silver solution followed by UV irradiation in a special box containing strong UV lamps. In order to ensure the treatment of the internal surface of the catheter, after dipping the catheters, the solution is forced by a syringe to flow inside the device and then it is expelled. The result after silver treatment is shown in Fig. 11.9 and, like the previous example of substrate, the polyurethane substrate also shows the typical browning due to the presence of silver on the surface.

After the silver deposition and an initial vigorous wash, scanning electron microscopy was carried on in order to verified the occurred photo-reduction of the salt and the uniformity of the coating on this type of substrate. SEM images are reported in Fig. 11.10 for the treated catheter, on the outer and inner surfaces, and for an untreated one. Due to the presence of small white inclusions in the untreated sample, an EDX analysis was combined with the SEM analysis in order to identify which particles were definitely silver. EDX has revealed the presence of elements belonging to the substrate and of barium, as expected, which is added in form of barium sulfate into the polymeric matrix to make it radio-opaque.

The amount of silver identified by EDS analysis on the treated catheter is slightly different between the internal and the external surface. The values obtained are 0.54 and 0.51 wt%, respectively for the external and the internal surface of the device. The reason for this result is the different superficial roughness of the polyurethane and the major difficulty of the UV irradiation to reach the internal surface of the catheter. This hypothesis is confirmed by SEM images in which a good coverage of the polyurethane surface and a quite good distribution of small particles are visible on the external surface, compared with the smaller coverage of the internal surface. As expected, no silver traces were revealed in the untreated sample by EDX.

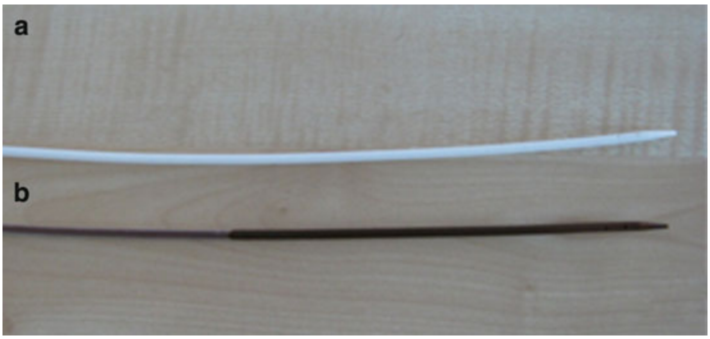

Fig. 11.9 Visual comparison of untreated catheter (**a**) and silver-treated catheter (**b**)

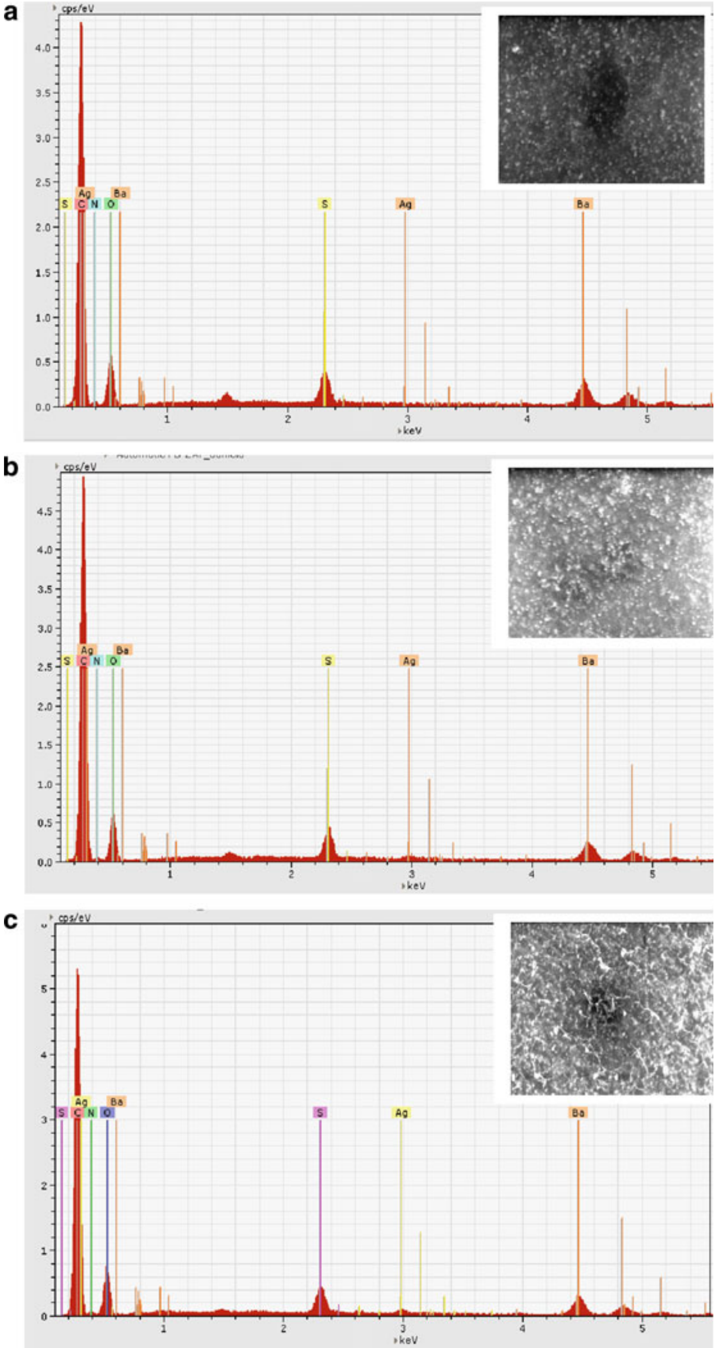

Fig. 11.10 SEM-EDX analysis on an untreated catheter (**a**) and a silver-treated catheter, on outer (**b**) and inner surfaces (**c**)

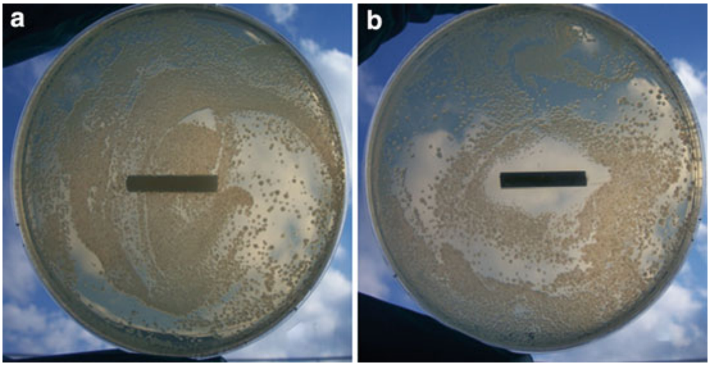

Fig. 11.11 Test of *Escherichia coli* growth on the silver-treated catheter (**b**) in comparison with the untreated one (**a**)

The antibacterial activity of silver-coated catheters was confirmed by an Agar diffusion test and a great inhibition zone to bacterial proliferation was observed, as shown in Fig. 11.11.

For this specific application, a strong antibacterial activity is required, so it is important to obtain a good compromise between the antibacterial capability and the amount of silver used for the treatment. The results of antibacterial test carried out on *E. coli* confirm that the small amount of silver used for the deposition is enough to ensure the inhibition of bacterial growth.

In order to evaluate the amount of silver, thermogravimetric analysis was also carried out and the data obtained are reported in Table 11.1. The value obtained is similar to the percentage of silver obtained by EDS and, in particular, it is 0.51 wt% for the treated catheter.

11.4.3 Silver Deposition on Leather Substrates

Public places and the public transport system represent an important field for the application of antibacterial technologies. The high number of users of trains, buses or taxies cannot guarantee a good degree of hygiene and welfare, causing allergies, dermatitis or skin irritation due to the proliferation of bacteria inside chairs or carpets. For this purpose, antibacterial coatings based on deposition of silver nanoparticles could represent an interesting solution to reduce such unpleasant consequences.

Substrates for public transport treated with Silvertech technology can be natural, such as the leather of chairs in trains and cars, and synthetic, such as polyurethane substrates for bus seats. For this work, synthetic substrates have been chosen and the adopted deposition process provides a roll coating in order to coat plain substrates of material more uniformly as possible. Moreover, this method makes it possible to treat just one side of the sample, that is the one in direct contact with people, with consequent reduction in costs. Synthetic leather simulates the microstructure of natural leather because the superfine fiber is similar to the fineness and structure of the fibril. The natural leather has a stereoscopic structure with the continuously changing degree of fiber cross-linking. The synthetic leather has a three-dimensional structure of superfine fiber non-wovens and microporous polyurethane. The uniform braiding structure of the synthetic leather is its advantage, but it is restricted technically by the lack of a grain layer. The chemical composition of the silver solution used for this application is made of a small percentage of silver salt dissolved in a mixture of water and alcohol. It is enough to be effective against bacteria and cheap at the same time. The amount of alcohol in the solution has to be directly proportional to the amount of silver salt, because alcohol represents the reducing agent that activates the photo-reduction, so the presence of at least a minimum percentage of it is necessary to guarantee the synthesis of the silver nanoparticles on the treated surface. The capacity to absorb the solution depends on the porosity of the substrates and, hence, changes of the colors of substrates also depends on it, being related to the amount of solution used for the treatment. Figure 11.12 shows images of a silver-treated sample and an untreated one, in which the difference in colors between them is not so great, due to the small amount of silver used for the deposition and to the nature of the substrate.

As for catheters, SEM analysis of synthetic leather has also revealed the presence of many inclusions on the surface of the sample, so EDS analysis was carried out during the scanning electron microscopy session in order to identify silver particles. The SEM images in Fig. 11.13 of the treated sample, carried at the low magnification of ×500, show a great porosity of the substrate and pores with different sizes and depths that influence the distribution of the coating. Some particles are visible on the side walls of pores and some larger aggregates are visible on the surface of the sample. The greater aggregates are not identified as silver, but they are more likely due to inclusions of other elements inside the synthetic leather, probably derived from the processing of the material.

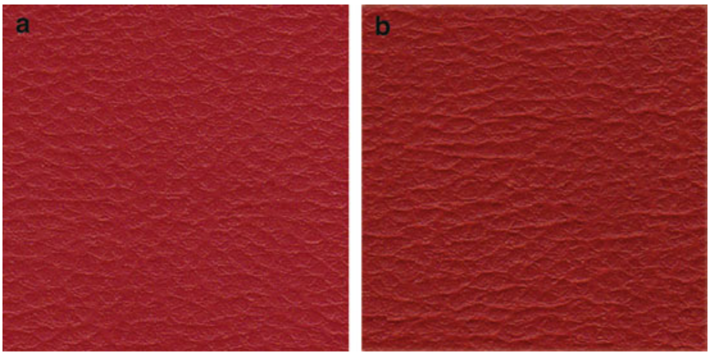

Fig. 11.12 Visual comparison of untreated synthetic leather (**a**) and a silver-treated one (**b**)

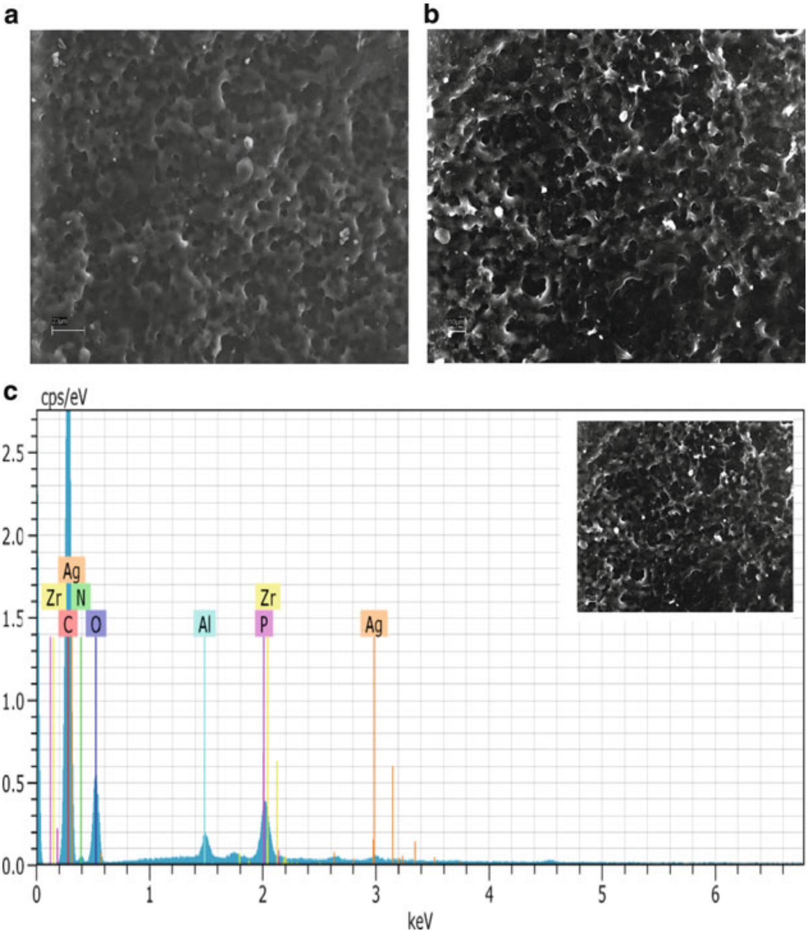

Fig. 11.13 SEM images on synthetic leather on an untreated sample (**a**) and on a silver-treated one (**b**) at low magnification and SEM-EDS analysis on a silver-treated sample (**c**)

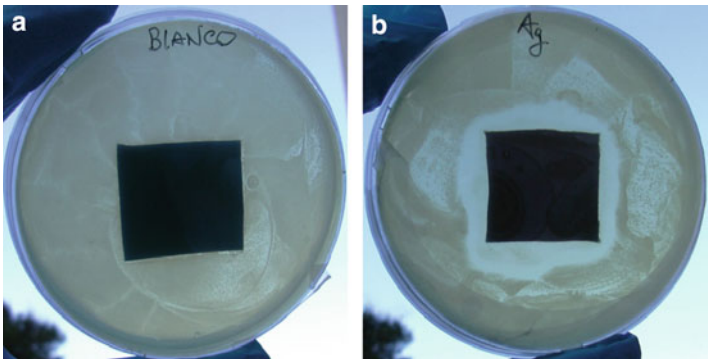

Fig. 11.14 Test of *Escherichia coli* growth on the sample of silver-treated synthetic leather (**b**) in comparison with the untreated one (**a**)

The antibacterial capability of silver-treated artificial leather was checked against *Escherichia coli* and the results are shown in Fig. 11.14. It was confirmed that silver particles on the surface reduce the bacterial growth on the sample, as visible from the comparison of the dimension of the bacterial growth inhibition area between the untreated sample and the silver-treated sample.

For this specific application of Silvertech technology, it is very important to satisfy both the antibacterial capability of the material and the necessity to limit costs. In fact, these substrates are intended to be used for a large number of external coverings for seats and chairs in public places, so the amount of silver has to be reduced in order to avoid increasing costs and ensuring at the same time a good reduction of bacterial proliferation. The amount of silver used in this example satisfies both the requirements. It has been calculated by thermogravimetric analysis, and the experimental data, reported in Table 11.1, show a percentage of silver corresponding to 3.08 wt%.

11.5 Conclusions and Future Trends

In this chapter, various properties and applications of antibacterial silver coatings have been reviewed.

In particular, an innovative and cheap technique to obtain antibacterial silver nanoparticles in situ developed in the University of Salento (Lecce, Southern Italy) has been described and discussed. The technology, suitable for many different types of substrates, consists of the photo-reduction of a silver salt in the presence of a reducing agent by UV illumination occurring directly on the substrate. According to the specific application of the substrate, the chemical composition of the silver solution (percentages of silver salt, alcohol, and water) and the method of depositing it on the material can be chosen in order to obtain the required antibacterial capability.

Three applications have been described in detail: antimicrobial textile, temporary implantable devices and artificial leather. For each of them, the silver deposition treatment and the experimental results obtained by the characterization of the treated substrates have been demonstrated. Despite the different natures of the treated substrates, it is possible to assert that the degree of coverage is good enough for each case and that there is a good distribution of silver nanoparticles on the materials. The small percentages of silver used for the treatment are enough to ensure a good antibacterial capability, as shown by the results of antibacterial tests carried out against *Escherichia coli*.

Experimental data revealed in this paper derive from many extensive studies carried out in applications in which this silver deposition technology can be considered ready for an industrial scale-up. One can expect that many other fields will be explored in order to extend the use of silver as an antimicrobial agent and to use it to improve health and welfare.

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